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Thermobaric and enhanced blast explosives (TBX and EBX)

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Abstract

In this review, excerpts from the literature of thermobaric (TBX) and enhanced blast explosives (EBX) that are concentrated on studies that include their compositions, properties, reactive metal components, modeling and computations are presented.

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1. Introductory

The last couple of decades have evidenced the emergence of a large number of weapon systems. Most warheads currently in service use explosives to throw metal fragments and/or shaped charge jets to destroy targets. Until recently, very few warheads relied on blast as their primary output. New technologies have been developed now for warheads that claim to possess enhanced blast performance.

Thermobaric weapons are classified as a subcomponent of a larger family of weapon systems which are commonly known as volumetric weapons. The volumetric weapons include thermobaric and fuel-air explosives (FAE, aerosol bombs in German). The term “thermobaric” is a compound word derived from the Greek words “therme” and “baros” meaning “heat” and “pressure” (implying the effects of temperature and pressure on the target), respectively. The characteristics of this category of weapons are mainly the creation of a large fireball and good blast performance [1]. Both thermobaric and FAE devices operate relying on some similar technical principles. In general, a thermobaric explosive (TBX) consists of a certain central charge (called the core), which is usually a high explosive, and an external secondary charge (fuel-rich formulation). Therefore, the detonation of TBX consists of a dual action: (1) Firstly anaerobic action (without air oxygen) inside the conventional high explosive core occurs; (2) Then aerobic delayed burning

action of the fuel mixture of the outer charge happens which depends mainly on the consumption of the surrounding air [2].

When a shell or projectile containing a fuel in the form of gas, liquid (aerosol) or dust explodes, the fuel or dust-like material is dispersed into the air which forms a cloud. Its occurrence does not depend on an oxidizer being present in the molecule. Then, this cloud is detonated to engender a shock wave, characterized with extended duration that produces overpressure expanding in all directions. In a thermobaric weapon, the fuel consists of a monopropellant and energetic particles [3]. In operation, the aerosol is detonated within a micro/millisecond in a manner similar to a conventional explosive like TNT or RDX. Meanwhile the particles rapidly burn in the surrounding air later in time, thus resulting in an intense fireball and high blast overpressure action.

Although the pressure wave, because of the explosive deflagration, is considerably weaker in comparison to a conventional explosive such as RDX, the fuel can rapidly diffuse into tunnels, caves or bunkers, producing considerably high heat effect for habitants and/or ammunition.

The explosion of an aerosol bomb consumes the oxygen from the surrounding air (the explosive composition usually does not possess its own oxidizer). In contrast to general belief of layman, its deadly effect is not simply due to the lack of oxygen caused but because of barotrauma of the lungs arising from negative pressure wave following the positive pressure phase of the explosion.

Thermobaric weapons contain monopropellant or secondary explosive and additionally possess elements like B, Al, Si, Ti, Zr and C, mostly [1–5]. After the explosion of the main charge

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of a thermobaric/enhanced blast explosive (TBX/EBX) occurs, the post-detonation reaction (namely, burning of Al, etc.) takes place with air, producing a huge “fireball” within a microsecond.

Russia was the first country managed to develop such kind of weapons. RPO-A Schmel rocket, infantry flame-thrower tested successfully in 1984, was the first thermobaric weapon which contained a self-deflagrating mixture consisting of magnesium (Mg) and isopropyl nitrate (IPN). This simple thermobaric explosive produced high devastating pressure wave through the Afghanistan caves and tunnel systems, causing huge damages in the subterranean mazes of the region [4].

The shock waves of conventional explosives are localized and substantially decrease while moving away from the explosion center. Thus, the conventional explosives have quite limited effects on fortified individuals, hiding inside bunkers and/or caves, etc. [5]. Recently, some thermobaric explosives (TBX) which are particularly highly metal-based systems have been successfully designed to exploit the secondary combustion which is responsible for the sustained overpressure and additional thermal effects [6,7]. During the detonation, ideal molecular high explosives (HE) (such as 2,4,6-trinitrotoluene (TNT), cyclo-1,3,5-trimethylene-2,4,6-trinitramine (RDX), pentaerythritol tetranitrate (PETN), and cyclotetramethylene tetranitramine (HMX)) all generate fast decaying blast waves of high peak pressure but very short duration and are mainly designed for either to throw shrapnel and shatter structures and/or penetrate armors. However, their effects are lethal only within their close vicinity and possess obvious undesirable shortcomings for destroying hardened targets such as caves, tunnels, etc. In order to overcome these shortcomings, great efforts have been spent on the development of new weapons which are able to generate higher blast, higher impulse and capable of using its energy not to destroy corners or walls only, but to travel around them efficiently and collapse the hardened targets [8].

In confined spaces, TBXs can become a source of lethal energy against soft targets [8]. They exhibit a highly pronounced effect as they are able to add to the total impulse within a fraction of a millisecond inside a building or up to one second within a tunnel [8]. Because of this, TBXs have received great attention recently. The fuel burning via reaction with the detonation products (after burning using oxygen from the air) raises the temperature of the gaseous product cloud as well, and meantime strengthens the shock wave [8,9].

The need for advanced thermobaric explosives have become one of the urgent requirements when the aim is focused on destruction of targeted fortified structures, caves and bunkers. Some highly metal-based systems have been designed to exploit the secondary combustion involved and resulted from active metal particles they contain. Hence sustained overpressure and additional thermal contribution can be achieved.

Barcz and Trzcinski reviewed some aspects of thermobaric and enhanced blast explosives [10]. Therein, the thermobaric and enhanced fuel explosives are defined and categorized as liquid and solid mixtures, and advanced compositions including layer charges. In the article the explosive formulations are char-

acterized in detail, and the methods used for determination of explosion parameters as well as the results of experiments and computer simulations are presented. The attention is particularly paid to understanding of the physical phenomena accompanying the detonation process in such heterogeneous compositions with a significant surplus of fuel [10].

In another article, Trzciński and Maiz reviewed the available literature on thermobaric explosives and enhanced blast explosives (high-destructive explosives) [8]. In their article, these types of explosives are defined, and their common features and differences were shown. Special attention was spelled onto the physical phenomena accompanying the process of explosion of such fuel-enriched heterogeneous explosives. They classified these materials as liquid and solid mixtures and composite materials, including layered charges as in their previous article. The considered explosives were characterized in detail, methods of determination of their blast parameters were discussed and the results of experimental tests were presented [8].

2. Thermobaric and enhanced blast explosives (TBX and EBX)

Since the differences between TBX and EBX are usually small, these two terms are therefore often interchangeably used in the literature. However, EBX types are primarily used to strengthen the blast wave, while TBX are employed to increase temperature and pressure of the explosion [8]. Both in EBX and TBX, some anaerobic and aerobic reactions occur. However, in EBX formulations, the metallic fuel reacts mostly in the anaerobic stage without participation of the oxygen from air, thus resulting in an important energy liberation which participates in the process of sustaining the initial blast wave and impulse, whereas in TBX, the aerobic metallic reactions dominate and the liberated combustion energy produced yields a moderate pressure and high temperature relatively for a long time in the last stage of the explosion after the detachment of the shock wave. On condition that the fundamental physical and chemical phenomena of TBX and EBX can be understood clearly and controlled consistently, brand new weapons of significant efficiency can be assembled. Then, a series of weapon systems may be available in the future.

3. Formulation strategies

There has been a long bygone of studying the blast explosives, reactive metals and associated metal combustion technologies. The achievements of the development of Solid Fuel-Air-Explosive (SFAE) have been demonstrated by a 30–40% increase of internal blast over a conventional explosive. SFAE is a singular event having combined mixing and initiation of the reaction. In confined spaces, if the solid fuel is ignited early in the dispersion process, transition to full detonation is not a requirement for enhanced blast occurrence. A series of reflective shock waves generated by the detonation leads the hot detonation gases and metal particles to be mixed and the metal particles are compressed at the same time. These actions provide certain chemical kinetic support to maintain a hot environment, thus causing more metal to ignite and burn. This

later-time metal combustion process produces a significant pressure rise over a longer time duration (10–50 msec). This phase is generally referred to as after burning or late-time impulse which can occur outside of where the detonation occurred and is responsible for more widespread damage.

Aluminum has been used as the metal of choice, due to its high heat of combustion, cost and availability. Billets of SFAE made of aluminum provide savings in volume with increased fuel mass for blast performance. However, combustion efficiency has been an issue to be handled, especially in the case of high fuel content (35–60 wt%) with respect to the total weight of explosive composition. Often poor combustion efficiency is observed in many of the thermobaric warhead tests, which means the severe ineffectiveness of the weapon. This is due to the high ignition temperature, 2200 K, which is the typically required temperature for the proper combustion of aluminum. As it is known, during the burning of aluminum, heat is produced and aluminum oxide (Al_2O_3) is formed. However, the complete burning of all the metal requires maintaining the environment's hotness [11]. This requirement can be best fulfilled if it is supported chemically by the combustion of other oxidizer species (i.e. AP or liquid nitrate ester, IPN (isopropyl nitrate)) that are much easier to ignite (AP has an ignition temperature of 250 °C and IPN has a low flash point of 22 °C). In operation, the combustion of these additives produce hot gases which support the burning of metal, thus 100% combustion efficiency can be attained. Metal composites, metal and oxidizer combined granules used in these explosives can be produced easily from coating of particles with a binder with well known techniques in the art [11,12].

In order to improve the metal combustion efficiency further, more reactive metals as part of or as the entire metal fuel components are used. New reactive metallic materials such as nano-sized aluminum to increase the reactivity, titanium and boron alloy to improve the thermal output, and magnesium/aluminum alloy to lower the ignition temperature are among the most promising and favorable approaches to increase the overall efficiency of metal combustion. More powerful explosives such as CL-20, TEX, etc. that are capable of elevating the detonation pressure and temperature are also shown to be extremely beneficial [11]. There exist some demand and interest in order to get new explosive formulations with new reactive metals and metal composites to have 50–100% higher blast energy as compared to composition such as those of Tritonal or PBX N109. Furthermore, the research for new formulations and new warhead designs are expected to produce more powerful thermobaric warheads in the future as compared to the already existing weapon systems.

4. Operational stages and amendments

Blast weapons could have been designed to fill a gap in capability; they are generally used for the attack of “soft” targets including personnel, both in the open and within protective structures. With the increased number and range of these weapons, it is likely that military forces will have widespread use of them in future conflicts.

Thermobaric explosives are generally fuel-rich compositions containing a nitramine (RDX, HMX, etc.), but they are characterized by the energy release occurring over a longer period of time than standard explosives, thereby creating a long-duration pressure. It is generally believed that the thermobaric explosives undergo the following stages upon detonation. In the first stage, an initial shock (or blast) wave from the explosive causes the nitramine to undergo anaerobic detonation (essentially a reduction reaction) occurring within hundreds of microseconds to disperse the fuel particles. The anaerobic combustion of fuel particles occurs in a second stage within hundreds of microseconds [12]. The anaerobic combustion process happens along the detonation shock wave while consuming fuel particles in close proximity to the detonating nitramine. In the third stage (afterburning), the fuel-rich energetic material is subjected to aerobic combustion, which is initiated by the shock-wave-mixing with oxygen of the surrounding air and which lasts several microseconds. The nitramine residues are preferably present in the shock wave and undergoes anaerobic reaction with the fuel particles to propagate the shock wave and increase dispersion of the fuel particles [12].

When the explosion takes place in an airtight environment, the energy release of the afterburning process can be subdivided into four types:

- 1) Earlier reports and articles [13–15] suggest that the metal powder in TBXs absorbs heat but does not release energy on the detonation wave front. The reflection of metal powder with the detonation products causes the first kind of afterburning.
- 2) The metal and the detonation products react with oxygen of condensed air. Because of the large density gradient, the R-T (Rayleigh–Taylor) instability turbulent flow is considered in order to explain this mixture and burning step [16,17].
- 3) The air detonation wave, reflected by the wall of the airtight environment, reacts with the high speed fireballs generated by the above process. Burning by the turbulent flow [18–20] is increased and the boundary temperature of the fireball rises to reignite the mixture of the metal and the detonation products.
- 4) The burning ball crashes to the barriers or the walls [13,17] and the kinetic energy of the medium in the ball is transferred into potential energy. The residual metal powder present may be ignited to form a new burning region. Of these four types, it is believed that the afterburning begins with the start of the detonation. It does not stop and even gets intense until the detonation processes finish. The fireball and the blast produced in the earlier stages are capable of reaching and turning corners and penetrate areas inaccessible to bomb fragments. Blast waves are intensified when reflected by walls and other surfaces, causing more intense damage effect of TBXs as compared to that of high explosives in confined conditions. The confined condition is important for TBXs. A limited space may be beneficial for the rising of

temperature and pressure produced by the reactions. In contrast the temperature and pressure cannot be held or even reduced in the open environment, thus the result of damage decreases and may be inferior to the equally conventional high explosives.

Thermobaric explosives typically are plastic bonded explosive (PBX) compositions, in which typically a metallic fuel and an oxidizer or a nitramine are contained. However, one drawback associated with the use of a PBX composition in a thermobaric weapon exists; that is, sometimes incomplete combustion of metallic fuel occurs [12]. Due to the diminished return of increasing fuel content, the fuel content is regulated so as not to exceed 35 weight percent. More typically it is maintained within a range of 20 to 35 weight percent. Due to this low fuel content, most successful traditional thermobaric weapons have been designed which are relatively large in size to furnish adequate fuel. Then, weight and size constraints accompany the large size and weight of such weapons. Although decreasing the size of the weapon can overcome this drawback, smaller thermobaric weapons tend to generate insufficient overpressure to destroy targets “in the open”. It is also believed that TBX compositions generally act like “high” or “underwater” explosives and they are characterized by shock-propagated reactions. Note that shock propagated reactions can bounce off of walls and succumb to rarefaction in closed spaces. The shock wave rarefaction causes a high degree of mixing and multiple reactions, thus it can limit the effective range of the thermobaric explosive, especially in closed or labyrinth-like spaces such as multi-room buildings or caves.

On the other hand, Dearden not only briefly describes fuel-air explosive blast weapons but reviews a range of enhanced blast weapons that have been recently developed [21]. Additionally he discusses on the reasons why enhanced blast technologies may be proliferating. Also approaching the subject from a different side he comments on how those explosives could affect the Defense Medical Services [21].

5. Reactive metals and metal carbonyls

Yen and Wang reviewed several classes of reactive metals that have been considered for energetic applications [2]. These include elemental metals, thermites/intermolecular composites (MIC), encapsulated metals, metastable alloys and “surface activated” metals. Properties, processing techniques, ignition and combustion characteristics of these materials as well as their field performance of the reactive metals in explosive formulations were also reported (if available). Finally, some reactive metals were identified in their review as potential metals.

Metals having high combustion enthalpies attract attention as high energy density materials. One of those metal additives is aluminum. Since the beginning of the 20th century aluminized explosives have been used in various formulations (e.g. Ammonal, Tritonal, Hexal, aluminized plastic bonded explosives, etc.). However, the potential benefits expected from aluminum additives have not been fully exploited. This is mainly due to the character of aluminum (the high melting point having oxide layer covers the surface, thus causing long ignition delays

and slow combustion rate). Hence, researchers have attempted to overcome these drawbacks by improving material processing and searching for new materials. One of these material processing techniques is the mechanical activation (MA) which is a size reduction process by milling techniques. Note that fine particles are usually more reactive than relatively coarse ones. Reactive metals find application in air-blast and underwater explosives. Due to the high heat released from reactions of metals with the decomposition products of explosives in ambient air or water, a considerably huge increase in energy release can be achieved. The active metal particles react over a much longer timescale than the detonation of the explosive itself. Thus, they contribute a great deal to the work done by the expanding combustion products. It is known that in underwater applications, the reactions of metals with water also contribute to the bubble energy [2].

In the past, not many other elemental metal powders besides aluminum are taken into consideration for the formulation of explosives. Quite recently, boron has been considered for the same purpose. The literature indicates that boron has the highest gravimetric and volumetric heat of combustion compared to aluminum and many other metal fuels. When boron was incorporated in HMX-based explosive compositions (B/HMX), it was observed that slightly higher explosion heats (per unit mass) occur compared to aluminum-containing ones (Al/HMX) in a bomb calorimetric test [22]. Lee et al. [23] studied the use of mixtures of boron and aluminum in an explosive formulation (RDX/Al/B/HTPB, 45/10/20/25). The test was conducted in a confined chamber and quasi-static pressure was measured. Note that a quasi-static process is a thermodynamic process that happens slowly enough for the system to remain in internal equilibrium. The authors found that the formulation containing mixtures of boron and aluminum performed 1.3 times better as compared to the formulation containing pure aluminum (RDX/Al/HTPB, 45/38/17). This is the result despite the lower metal content. Therefore, it appears that boron is a potential candidate for use as fuel additive in energetic compositions. Nonetheless, there is also some experimental effort indicating that the high ignition temperature of boron is actually a drawback to its application [24]. Since the boron flame temperature is 2067 °C, while its boiling point is 3865 °C, boron burns at the particle surface, which consequently turns into a covered surface coated with the viscous oxide (B₂O₃) at such a high temperature. Because of that, this occurrence reduces the ability of the fuel to mix well with oxidizer and leads to inefficient burning. Schaefer and Nicolich studied the blast performance of boron-containing cast-cured, HMX-based explosive in a semi-confined structure [25].

The results showed that the use of boron decreased the impulse by half when it partially replaced a MgAl alloy powder [25]. Although the paper did not offer any explanation for its poor performance, it is likely that the long ignition delay of boron caused it to act as an inert diluent to the resultant overall explosive effect. Therefore, unless the ignition temperature can be lowered considerably (through the use of some appropriate chemical/physical processes) the full potential of boron cannot be harnessed [25].

Various reactive metals (Mg, Al, Ti, Zr) have also been tested as incendiary warheads for a penetrator by Sandia National Laboratories [26,27]. Titanium and zirconium, which are denser metals than magnesium and aluminum (a desirable factor for penetrators), were tested in various forms (gravel, washer, sponge). The configuration of the test charges were designed in such a way that cylindrical reactive metal casings (with and without external steel case) filled with a high explosive core. The charges were initiated in a test cell, which consisted of paper, newspaper, wood and plywood, and empty propane tanks. The course of detonation, dispersion of particles and additional effects were monitored by a video camera. From the qualitative results of these tests, it was found that zirconium is the best incendiary metal. It was capable of starting fires inside the test cell causing lots of damage. Due to the numerous parameters such as explosive core, mass of explosive, % TMD of the casing, etc. (that were varying in the test) direct comparisons were found to be difficult.

Although many reactive metals until now have been studied in terms of combustion and ignition kinetics, field performances of reactive metals in explosives are scarce. Based on the limited reports available, the charge configuration, charge sizes and test conditions are also different and hence cross comparison of the effects of reactive metals are difficult. However, based on this review, it is apparent that some reactive metals could potentially perform better than aluminum [28]. Metastable alloys also can have high heat releases, exceeding that of aluminum, and approach those of boron. Metastable alloys also have lower ignition temperature than pure metals. Dreizin et al.'s work indicated that Al-Mg (50 wt%: 50 wt%) and B-Ti (25 wt%:75 wt%) were found to be the most promising mechanical alloys based on constant volume combustion chamber experiments [28].

On the other hand, encapsulating aluminum with reactive metals such as magnesium, zirconium, and nickel or with polymers such as Teflon, Viton, and NC would also lower the ignition temperature and bridge the gap between microsecond detonation reactions and millisecond burning reactions. Thermites also may be used in some cases where obviously there is oxygen deficiency. For greater energy, fuel-rich aluminum-based thermites can be employed [2]. The availability/proximity of oxygen (by creating an intimate mix between the oxide and the metal particle) will ensure a better composition of aluminum. Of the thermites tested, Al/MoO₃ shows the greatest potential among the others because it has the highest gravimetric heat of compositions and the lowest activation energy and ignition temperature. However, the challenge is to obtain spherical or near spherical forms of these reactive powders so that they could be loaded to high solid content (density) in explosive formulations.

It is worth mentioning that not only aluminum but recently some other metals have been used in thermobaric/enhanced blast explosives in different forms such as magnesium, magnesium-aluminum, aluminum (Alcan, Alex), boron, coarse and fine silicon, titanium, and zirconium, etc. [29–32]. Also Chan and Meyers studied nanoparticle aluminum, boron, titanium, magnesium, Al-Mg, hydrided Al-Mg, B-Mg, Al-B, and Ti-B alloys as fuels [11].

On the other hand, Kellett studied bimetallic particles composed of a core/shell structure of differing metals. The core metal is from aluminum, boron, silicon, hafnium, magnesium, or carbon, whereas the outer shell metal is from nickel, boron, titanium, zirconium, sulfur, selenium, or vanadium [33]. Hafnium and zirconium show promise as incendiary materials and for application in reactive fragments. However, their extreme electrostatic discharge sensitivities (ESD) impose significant safety issues that limit their usage in energetic applications. Because of this, aluminum-coated hafnium and zirconium were developed to lower down the sensitivities of these metals to that of aluminum level [2]. Aluminum or boron can be coated with more active metals such as magnesium to improve the ignition temperature and the combustion time. A suitable technology has been developed for coating a high-melting-refractory-metal with a low-melting soft metal and has applied the product, such as magnesium-coated boron, for energetic applications. Boron, due to its high heat of oxidation and low atomic weight, is one of the highest energy density materials known. Unfortunately, it is very difficult to ignite due to its inherent reactivity and oxide-surface-coating, whereas magnesium, by comparison, is relatively easy to ignite, and by coating boron particles with magnesium, the ignition characteristics are substantially increased. In this application, the burning of magnesium heats the boron particles, and keeps the surface relatively clear of formation of boron oxide, which is a viscous liquid at high temperatures and thus hinders the reaction [2].

On the other hand, Zimmermann studied transition metal carbonyl complexes as blast enhancers and boosters for hollow charge explosives in order to improve burning [34]. The carbonyls tested consist of Cr(CO)₆, Mo(CO)₆, W(CO)₆, Fe(CO)₅, Fe₂(CO)₉, and Fe₃(CO)₁₂ [34].

6. Mechanism of action

Fuel-air explosives (also called thermobaric explosives/weapons) with organic fuels have been known since the 1960s. Such composites have a high negative Gibbs free energy of reaction, but exhibit only a moderate detonation pressure [35,36]. However, due to an enhanced impulse, the blast effect of such explosives is much higher than that of ordinary high explosives. In fuel-air explosives atmospheric oxygen is used as an additional oxidizer for the explosives. Therefore metal fuels having high negative Gibbs free energy per mole of consumed oxygen (e.g. Al) are also used as additives in thermobaric explosives. When a warhead detonates, for instance inside the hull of a ship, in the first-hand the ship hull experiences a shock loading and then a quasi-static pressure develops. The latter is considered a determining factor for the structural damage. Optimal performance is achieved when the quasi-static pressure is sufficiently high to destroy the dividing walls present between the compartments of the ship structure. Afterburning may subsequently occur by reactions with oxygen in the available air in the neighboring compartments [30,37,38]. A proviso for this event is that the Al content and particle size will not reduce the effects of fragments in a significant way. In open air, the afterburning becomes far from complete due to the rapid expansion, thus cooling of the fireball ensues. When the reaction

products expand and mix turbulently with the air, the temperature of the gases decreases rapidly, thus leading to incomplete combustion process. Therefore, small metal particles are to be preferred because they burn faster. Trzcinski et al. studied blast waves and found that the maximum impulse occurred at an aluminum content of around 30%. The peak value was reported as approximately 15% higher than that of pure RDX [39]. Furthermore, they asserted that the overpressure peak of the incident wave was comparable to or lower (by 5 to 17%) than that of RDX. The conclusion was that in general the blast performance was only slightly increased. However, it has been shown that for a gelled based metal-enhanced fuel-air explosive (metal content of approximately 60%), air blast surpasses the energy density of conventional propylene oxide fuel-air type explosives. TNT equivalents of about 500% have been observed [30]. Note that enhanced-blast weapons are primarily designed and effective to demolish bunkers, caves and enclosed structures (see Reference [40] for a review of thermobaric weapons).

Transition to full detonation is not required in confined spaces to achieve an enhanced blast. When an explosive charge detonates in a closed chamber reverberating waves (for a short time) determine the pressure-time history in the chamber. After several reflections an equilibrium pressure is reached, on condition that there is no heat loss to the chamber during this short period of time.

In addition, for confined space and low loading densities sufficient oxygen is available in the air to complete mixing. The post-explosive temperature is commonly between 2500 K and 4000 K in confined spaces, and remains high for a long time, allowing the explosion products and the available air to reach a thermodynamic equilibrium (the optimum aluminum content for maximum blast effect is then at least 50%). These results for confined spaces are probably also applicable to conditions where the confinement is not entirely complete (e.g., a detonation chamber is connected to the open air by a tunnel).

However, for semi-confined explosions, the conclusion is not so obvious. It is conceivable that walls will be blown out before aluminum will be appreciably mixed with air and oxidized. Then, the energy of explosion depends on the available air oxygen to an extent which is related to the oxygen deficiency. The addition of about 40% aluminum to high explosives like RDX or HMX leads to a significant enhancement of the calorimetric heat of explosion (also called energy of explosion or energy of detonation) [39]. This enhancement is typically around 40%, which is substantially lower than predicted from the theoretical calculations.

Furthermore, a set of explosions has been performed in a closed chamber having different atmospheres in order to estimate the degree of afterburning of the detonation products in confined or semi-confined chambers. It has been found that the quasi-static pressures in closed compartments are much lower than the thermodynamically calculated values, but may be around 20% higher than of pure RDX when 45% Aluminum is added. The pressure is indeed much higher than the pressure calculated by the assumption of inert aluminum. This result indicates that it reacts with oxygen from the air in the chamber as well as with RDX decomposition products [39]. It has been

found that the quasi-static pressure in a chamber filled with air is higher than the case if the chamber is filled with nitrogen or argon. The analyses of the chamber residues after detonation (0.15 m³ chamber, 200 gram explosive) have revealed that only in air, alumina constitutes the residues entirely. This means that the aluminum that has not reacted in the detonation/combustion wave is fully oxidized in expanding and re-shocked RDX products, meanwhile consuming oxygen from air [36].

7. Composition and characterization

Various studies have shown that solid state fuel-air (enhanced-blast or thermobaric) explosives seem to have very promising features. They can combine metal fragmentation and metal acceleration effects with superior air blast impulse. Thus the consequence is much better ordnance with improved effectiveness and combined modes of action on the targets.

Kolev and Tzonev presented the results of their practical solutions to these problems in two types of solid state thermobaric explosives [41]. They have air blast TNT equivalent of about 2.5 times and metal fragmentation capabilities similar to that of TNT. Both types of compositions mentioned are thermally stable, cheap and technologically accessible for mass production.

A widely used fuel in energetics is the micrometer-sized aluminum. However, performance of propellants, explosives, and pyrotechnics could be significantly improved if its ignition barriers could be disrupted. Sippel et al. reported the morphological, chemical and thermal characterization of fuel-rich aluminum-polytetrafluoroethylene (70–30 wt%) (Al-PTFE) reactive particles formed by high and low energy milling [42]. Average particle sizes of their samples ranged from 15 to 78 μm ; however, the specific surface areas of the particles ranged from approx. 2–7 m²g⁻¹ due to milling induced voids and cleaved surfaces. The SEM and energy dispersive spectroscopy revealed a uniform distribution of PTFE, providing nanoscale mixing within the particles. The combustion enthalpy was found to be 20.2 kJ g⁻¹, though a slight decrease (0.8 kJ g⁻¹) results from extended high energy milling due to $\alpha\text{-AlF}_3$ formation (note that PTFE is present). For high energy mechanically activated particles, differential scanning calorimetry in argon atmosphere exhibited a strong peak standing for the exothermic pre-ignition reaction that onsets near 440 °C and accompanied by a second, more dominant exotherm that onsets around 510 °C. Scans in O₂-Ar atmosphere have indicated that, unlike physical mixtures, more complete reaction occurs at higher heating rates and the reaction onset is drastically reduced (approx. 440 °C). The simple flame tests reveal that these modified Al-polytetrafluoroethylene particles light readily unlike micrometer-sized aluminum. Safety testing also shows that these particles possess high electrostatic discharge (89.9–108 mJ), impact (>213 cm), and friction (>360 N) ignition thresholds. The data imply that these particles may be useful for reactive liners, thermobaric explosives, and pyrolants. In particular, the altered reactivity, large particle size and relatively low specific surface area of these fuel-rich particles make them an interesting and suitable replacement for aluminum in solid propellants.

This work clearly shows that mechanical activation of fuel rich Al-PTFE mixtures can result in micrometer-sized Al-PTFE composite particles with increased reactivity. The authors have observed that use of mechanical activation process results in nanoscale mixing of reactants with reaction behavior similar to that of nAl-nPTFE. Notably, high or low energy mechanical activation results in significant shift of primary exotherm onset from 600 °C to 440 °C in anaerobic heating and from 540 °C to 440 °C in the presence of O₂ [42]. For composite particles formed with high energy mechanical activation, differential scanning calorimetry in O₂-Ar indicates that, unlike physical mixtures or those particles formed under low energy mechanical activation, more complete reaction occurs. At higher heating rates the reaction onset is also drastically reduced (approx. 440 °C). Furthermore, results suggest that at aerobic heating rates, greater than 50 K min⁻¹, nearly complete heat release happens approximately at 600 °C instead of at higher temperature. While mechanical activation drastically alters the reactivity of these particles, they are relatively insensitive to electrostatic discharge (ESD), friction initiation and impact. In addition to having significantly modified reaction behavior, the enthalpy of combustion of mechanically activated particles was found to be as high as 20.2 kJ g⁻¹, so that it is approximately 60% higher than the measured combustion enthalpy of nAl-nPTFE mixtures. Additionally, the large (15 to 78 μm) average particle size and moderate specific surface areas (2 to 6.7 m²g⁻¹) of composite particles suggest that they will be far more useful than nanoparticles in high solids loaded energetics and may age more favorably than nanoparticle mixtures. Their expectation is that further reduction of particle specific surface area helps improvement of aging characteristics which may be achieved by adding a small amount of binder (e.g., Viton A) during the milling process or through crash deposition after mechanically activated particle formation. The conjecture is that a lower fraction of PTFE may also prove to be advantageous for some applications. These micrometer-sized activated fuel particles with modified ignition and reaction characteristics are a promising alternative to nanoparticle solid propellant additives such as nAl. With these particles, the authors expect similar propellant performance improvement and particles becoming less detrimental to propellant rheological and mechanical properties. When used as a replacement in solid propellants, these particles may ignite far below the ignition temperature of micrometer-sized aluminum (>2000 °C) and the expectation of the authors is that with these particles they may decrease ignition delay, agglomerate size, and reduce condensed phase losses as well as lead to increased heat output and enhanced burning rates [42]. Use of these fuel-rich Al-PTFE composite particles in structural energetics (e.g., reactive liners), incendiaries, flares and other energetics could also likely lead to better performance, far exceeding that of energetics which are made from physical mixtures of micrometer- or nanometer-sized particles. Now, efforts have been focused on the use of other fluorocarbon oxidizers. Study of the ignition and combustion of these activated fuel particles at high heating rates is interesting too. Additionally Sippel et al. have been working to incorporate these materials into solid and hybrid propellants [42].

On the other hand, Simic et al. in their paper describe the effects of compositions on the detonation properties and the parameters of the air shock wave front on a lightweight model of cast thermobaric explosives (TBE, 400 g) [29]. This investigation comprises 14 thermobaric explosive compositions containing HMX, AP, Al, Mg, HTPB (hydroxy-terminated polybutadiene binder) in different weight percentages. Theoretical and experimental densities and porosities of TBE charges and detonation velocities were determined. Depending on the content of explosive, binding and component compositions, as well as on the content of Mg/Al as a fuel, the basic parameters of the shock wave speed, overpressure (Δp), maximum pressure ($P_{ut,max}$) and TBE pressure impulse values were determined at different distances from the explosion center. By using piezoelectric pressure transducers, examination of the thermobaric effect was performed by means of measuring overpressure in the shock wave front. The activation and the detonation of explosive charges as well as the expansion process of detonation products were filmed by a Phantom V9.1 high speed camera [29].

For the needs of investigation of the effects of composition on the detonation properties and the parameters of the air shock wave front, new compositions of cast composite thermobaric explosives have been developed having the mass fraction of components: 31–50% of HMX, 15–20% of HTPB-based binder, 21–30% of Al, 0–9% of Mg and 0–20% of AP (ammonium perchlorate). In the study 14 experimental TBE compositions were prepared. The influence of the compositions and the ratio between the components on the detonation properties and the parameters of the air shock wave were examined each time, on light-weight experimental models (~400g). The test results were compared with the parameters of the standard charge (HMX/Al/HTPB = 50/30/20). The maximum overpressure values at all measuring points were achieved with TBE-3 (45% HMX, 10% AP, 21% Al, 9% Mg, 15% HTPB) and the lowest ones with TBE-1 (50% HMX, 30%Al, 20% HTPB). At greater distances from the explosion center, small differences in the values of the maximum overpressure were recorded which were indicative of the influence of the composition on P_{max} values which had the most pronounced value in the area nearby the detonation site. It has been obtained that all the compositions containing magnesium had higher values of overpressure as compared to the standard charge. All the new compositions have higher pressure impulses than the standard charge. Among these, the compositions named as TBE-3, TBE-7, TBE-12 and TBE-1b are outstanding. They all have a higher content of the explosive component, aluminum, and have combined with a greater percentage of magnesium. The TBE-3 composition possesses the most favorable characteristics of thermobaric explosive in comparison to the other investigated compositions. It is characterized with higher detonation velocity, higher overpressure and pressure impulse; thus it can be recommended as the composition of choice for further research along this line [29].

Also the effect of the composition of cast composite thermobaric explosives on their processability was investigated by Simic et al. [43]. According to the experimental plan, 10 different thermobaric PBX explosive compositions (containing

HMX, AP, Al, Mg, HTPB binder in different mass percentages) were prepared by applying the casting technology. The content of three components was varied: thermosetting hydroxy-terminated polybutadiene binder (HTPB, 15–20 wt%), ammonium perchlorate (0–20 wt%), and magnesium participation in a total metal content of 30 wt% (i.e. 0–30 wt% of aluminum was replaced by pyrolytic magnesium). Both the impacts of composition and curing time on viscosity were examined. Then, how the changes of component content affect the viscosity-time dependence for the three (upper mentioned) components taken separately as well as combined was analyzed. The densities of the samples taken from different segments of explosive charges were determined according to the standard method MIL 286B, and then the porosities were determined as well [43].

Aluminum is commonly used as a fuel component due to its high heat of combustion, cost and availability. It has a high ignition temperature (2200 K). Thus, burning of all the aluminum to completion requires maintenance of the hot environment. It can be managed if it is supported by the combustion of other easily combustible metals and oxidizers. A representative example is ammonium perchlorate (AP). It is much easier to ignite AP (AP has an ignition temperature of 250 °C) compared to aluminum. The combustion of AP produces hot gases which support metal burning effectively, so that much higher combustion efficiency can be obtained. Nowadays, aluminum is used in mixtures together with magnesium for getting more complete combustion [11,44]. Magnesium, on the other hand, is capable of catalyzing some polymerization reactions. It is reported that it has some influence on HTPB polymerization [45,46]. HTPB was used as a binder in cast composite explosive compositions examined in this investigation.

The investigation of processability was done for 10 different thermobaric PBX explosive compositions, previously prepared. Throughout the study, viscosity-time dependences, densities and porosities were all determined for the examined samples. The mass concentration of the binder has the greatest effect on the rheological properties of the examined compositions, then the participation of Mg in the total metal content, and the concentration of fine aggregates of AP at the expense of reducing the content of coarse fraction HMX. A higher amount of Mg in compositions (with the same content of other components) causes faster growth and higher values of viscosity, thus reducing the processing time (castability) of the compositions, while a larger content of the binder and replacing HMX by AP have a favorable effect. For the selected representative compositions, the measured density values have shown to be very close to the theoretical values. There are also no significant variations between the values of density in different segments of experimental explosive charges. Thus, it can be concluded that a very good homogeneity has been achieved. The porosities of the examined explosives were low, which was a good qualitative property for this kind of explosives. The values of porosity are lower for the compositions containing a higher percentage of AP and Mg, and also having a higher content of the HTPB binder. The TBE-4, TBE-5, TBE-8, TBE-9 and TBE-10 compositions have a moderate viscosity gradient and therefore, good rheological properties. They all remain castable long

enough, so they have favorable processing characteristics; especially TBE-8 and TBE-9 are to be noted as having the lowest porosities after curing. Taking this into consideration as well as a good thermobaric effect that can be predicted based on their content of ingredients, the explosive compositions mentioned above represent good candidates for industrial production.

In the work of Newman et al., a pressable explosive composition was provided [12]. The composition included at least 40 wt% of substantially uncoated fuel particles, a nitramine which was mechanically blended with the substantially uncoated fuel particles, and a binder coating the nitramine. Also the article provided a pressed thermobaric explosive formulation, weapons compositions and methods for making the composition and the thermobaric explosive.

The pressed thermobaric explosive should preferably possess at least one, and still more preferably all, of the following characteristics: (a) a compressive strength greater than 42,000 psi, more preferably greater than 45,000 or 50,000 psi. (b) a frictional sensitivity less than 235 psig (more preferably less than 420 psig, as measured by an ABL sliding friction test); (c) a frictional sensitivity less than 360 N (more preferably less than 252 N, as measured by the BAM sliding friction test); and (d) an equal or lesser electrostatic discharge sensitivity than that of RDX.

The method provided in the article comprises coating a nitramine with a binder. The coated nitramine is mechanically mixed with substantially uncoated fuel particles in order to provide a pressable explosive composition comprising at least 40 weight percent of the substantially uncoated fuel particles (preferably about 1 to about 6 weight percent of the binder). The explosive composition is preferably consolidated via pressing to provide a pressed thermobaric explosive [12].

It is claimed that the substantially uncoated fuel particles preferably (yet optionally) possess one or more of the following properties: relatively low melting point, a high heat of combustion, high surface area (small particle size), and ammability. For the solid fuel particles, they are preferably kept dry in the processing and in the pressable explosive composition to maximize reactivity with air. The fuel particles are preferentially selected from a set of aluminum, magnesium, magnalium, and various combinations of them. Of these, aluminum and magnalium are particularly preferred. Note that magnalium is an alloy of magnesium and aluminum which is usually but not necessarily prepared in a 1:1 molar ratio. In the pressing step, magnalium is generally more difficult to consolidate than aluminum. Accordingly, a portion (e.g., 50 weight percent) of the magnalium is preferably preconditioned with a wax composition in order to improve its cast consolidation capabilities. A preferred embodiment is given as a portion of the uncoated magnalium fuel particles treated with Comp-D-2 Wax. Another example of a fuel particle is carbon powder, especially carbon powder containing at least 4 weight percent volatile materials. An example of carbon powder may include, not necessarily by limitation, bituminous coal and/or petroleum coke.

The selected nitramine should preferably have one or more of the following properties: (1) a high heat of combustion, (2) a high detonation pressure, and (3) a high detonation velocity.

In the article some representative nitramines, useful in the thermobaric explosive composition of the invention are suggested as, for example, 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo-[5.5.0.0.5'903'11]dodecane (CL-20 or HNIW). Of these, RDX and HMX are especially more preferred in use alone or in combination [12].

A thermobaric explosive composition provided by Baker includes coated fuel particles, a nitramine and a binder [47]. The coated fuel particles preferably have a magnesium core and an aluminum coating. Upon detonation, the nitramine disperses the coated fuel particles over a blast area during a first overpressure stage. The aluminum coating of the fuel particles has a suitable thickness so selected to provide the necessary amount of aluminum, namely, it should be stoichiometrically less than an amount of ambient-air oxygen available in the blast area for aerobic combustion with the aluminum during the first overpressure stage. Once exposed, the magnesium cores may combust to increase the impulse generated in the first overpressure stage. The article also provided some manufacturing techniques and related methods [47].

Smith described certain compositions that contain aluminum together with the high explosive HMX or RDX [48]. The compositions were manufactured safely by means of a water-slurry process, despite the fact that aluminum used reacts with water. The binder system that was investigated is HyTemperature together with dioctyladipate (DOA) as the plasticizer. This binder system was chosen because of its well-known good property for usage in preparation of insensitive munitions (IM). The process yields granules suitable for pressing and is characterized by composition, analysis, shape and bulk density. Also the pressability of the compositions was investigated as a function of the particle size distributions of the nitramine, the content of aluminum and the amount of binder. By using sensitivity-reduced crystals of HMX or RDX, the compositions showed a significant decrease in the shock sensitivity even though they were pressable compositions. This observation was in agreement with what had been observed also for other pressable compositions that were reported earlier. The water slurry process have also been used to obtain an analogous composition designated and named as PBXIH-18 that contains the same binder system [48].

Chan and Meyers described a solid fuel-air thermobaric explosive with improved combustion efficiency exerting a relatively high blast pressure in an oxygen-poor environment, such as a tunnel or other confined space [11]. The explosive considered consists of: (1) a first grain, comprised of a high explosive and (2) a second grain, of a metal fuel, in which the second grain surrounds the first grain, at a 0.66–1.45 wt. ratio of second grain to the first grain. The composition can also contain 4.0–6.0 wt% of a binder, and 14.0–36.0 wt% ammonium perchlorate. The first grain typically contains 87–90 wt% HMX, with energetic binders selected from hydroxy-terminated polybutadiene, hydroxy-terminated polycaprolactone, hydroxy-terminated polyethers, polyglycidyl azide, lauryl methacrylate, and trifluoroethyl-terminated poly(1-cyano-1-difluoroamino)-

polyethylene glycol. On the other hand, suitable metal fuels include nanoparticle aluminum, magnesium, boron, titanium, Al-Mg, hydrided Al-Mg, Al-B, B-Mg and Ti-B alloys.

Several different metal fueled thermobaric explosive charges were prepared and tested by Hahma and coworkers [30]. Four different metals, namely magnesium, magnesium-aluminum alloy, aluminum, and activated aluminum were selected as the metallic fuel. Additionally, different solid and liquid organic fuels were used as the initiating fuel. The dispersing charge was similar in all the experiments that contained plastic PETN (20% of the main fuel weight). In the experimentation the air blast pressure was recorded at four different distances. Then, the data were analyzed and TNT equivalences were determined. The charges that ignited the metal fuel were considerably more powerful than TNT while those showing weaker blasts often did not ignite the metal fuel at all.

To select the most efficiently enhanced blast formulations of the system containing Hexogen/Aluminum/HTPB, Gerber et al., in a first step, calculated the heat of combustion, the heat of detonation, and the difference of both the heat of afterburning [49]. The quotient of the heat of afterburning and heat of detonation and a minimum of the heat of detonation were useful factors to limit the possible formulations. A series of experiments were done in a combustion chamber and the results of pressure and temperature measurements were presented [49]. The inert binder HTPB was compared with the energetic binder GAP. Also the results of the enhanced blast formulations were compared with TNT and the composition called PBXN-109 [49].

Various methods to prepare insensitive enhanced-blast explosive molding powders were given by Newman et al. [50]. The experimental protocol consists of (1) suspending energetic solids and powder metals in a bulk fluid phase (e.g., a perfluorocarbon), (2) adding a polymeric lacquer to the suspension to produce a supersaturated solution of energetic solids and suspended metal powders, (3) final granulation to form a fluidized metalized energetic molding powder, and (4) distillation removal of the organic solvent portion of the lacquer to recover a wet metalized molding powder. The polymeric lacquer mentioned can be one containing an elastomeric thermoplastic. The bulk phase fluid is recovered through distillation. The wet molding powder is then dried to a powder containing a lacquer-polymer having weight ratio of 14–18:1. The patented work of Newman et al. considers explosive components including nitramines, oxidizers, nitrate esters, metals, and combustible powders, such as ammonium perchlorate, trimethylolethane trinitrate, composite double-base propellants, flaked aluminum powder, and bituminous coal powder [50].

The theory and performance for recently developed combined-effects aluminized explosives were reviewed by Baker et al. [51]. Traditional high-energy explosives used for metal pushing incorporate high loading percentages of HMX or RDX. The traditional blast explosives commonly used incorporate some percentage of aluminum. Although these high-blast explosives produce increased blast energies in explosion, they are normally characterized with reduced metal pushing capability, due to the relatively late-time aluminum reaction. On

the other hand, the combined effects aluminized explosives achieve both the excellent metal-pushing effect and high blast energies. The enhanced metal-pushing capability is because of the earlier exothermic conversion of aluminum to aluminum oxide as compared to the conventional blast explosives. Note that the traditional Chapman–Jouguet detonation theory with completely reacted aluminum does not explain the observed detonation states achieved by these combined-effects explosives [51]. It is demonstrated that eigenvalue detonation theory explains the observed behavior. Both the high metal-pushing capability and high blast are achieved by using these new explosives.

In order to quantify the contribution of aerobic and anaerobic aluminum reaction contributing to blast and overpressure, aluminized RDX-based explosives were detonated under controlled conditions while varying the particle size and atmosphere [52]. Early-time reaction of aluminum acts to enhance the primary explosive blast, and this reaction is approximately half aerobic and half anaerobic (i.e. compositions by detonation products and/or nitridation), suggesting that very rapid early-time mixing occurs in explosive fireballs. It was found that particle size effects were surprisingly negligible over the range of 3–40 μm . The observation implies that conventional scaling laws for aluminum combustion provide less insight than previously assumed. The data of quasi-static pressures obtained in the time period from 5 to 10 microns after detonation have revealed that oxidation of aluminum is complete in the presence of 20% O_2 . However, in N_2 environments, oxidation of aluminum only proceeds to half its theoretical maximum, except for the smallest particles (3 μm) for which oxidation was almost complete. Thus, oxidation of aluminum in aluminized explosives is robust in anaerobic environments. Therefore the simulation efforts cannot over-neglect the anaerobic channels, even though aerobic oxidation provides the greatest energy release.

In the article by Nicolich et al., high-performance aluminized explosive compositions for high performance, high blast, low sensitivity explosive applications have been presented [53]. The compositions include CI-20, HMX, RDX, or another material as the explosive ingredient, a binder system of cellulose acetate butyrate and bis-dinitropropyl acetyl and bis-dinitropropyl formal, and aluminum. The explosive is preferably pressable and or/mixable to permit formation of grains suitable for ordnance and similar applications including grenades, landmines, warheads, demolition, etc. It was found that the aluminum fully participated in the detonation of abovementioned explosive compositions, manifesting its energy into fully usable metal-pushing energy which is suitable for shaped charges, explosively formed penetrators, enhanced blast warheads, fragmentation warheads, multipurpose warheads, and so on. The aluminum is substantially reacted at two volume expansions of the expanding gas, and fully reacted prior to seven volume expansions of the expanding gas [53].

During the last couple of years, great efforts have been focused on the development of new kinds of weapons which are able to generate high blast and temperature effects, namely abovementioned thermobaric weapons. Also, a lot of research

studies have intensely focused on the comprehension of thermobaric effects, in order to enhance or prevent it. The blast effect is mainly due to the ability of the detonation products to react with the oxygen of air. This phenomenon called afterburning substantially contributes to generate high pressure impulses, especially in confined spaces. This is the reason why metallic particles, mainly aluminum particles, are commonly used in thermobaric explosive compositions (TBX). In the light of the recent studies, in France (SME Center de Recherche du Bouchet) a novel enhanced-blast plastic-bonded explosive (EB-PBX) has been developed in order to generate enhanced blast effects [54]. This new composition has been called B2514A. The developmental stages of such a composition have been performed through different phases, within the domain of small scale trials to large scale ones. A specific methodology was used to examine and classify a large number of candidates. The most promising composition experimentally has been tested at large scale to characterize its ability to generate blast effects in comparison with PBX known for their blast effects [54].

The reaction of metal particles with the decomposition products of energetic materials like water, carbon oxides and nitrous gases plays an important role in many pyrotechnics. Often, air that is entered into the fumes can also burn the metal particles or other reaction products in rival. This may lead to additional heat release, radiation or other desired effects in applications like ducted rockets, aluminized rocket propellants, blast-enhanced explosives (SIBEX), incendiaries or countermeasure flares, etc. In order to investigate such reactions, Weiser et al. considered a composite RDX, including 5% paraffin mixed with particles of various reactive metals: aluminum (Alcan, Alex), magnesium, boron, coarse and fine silicon, titanium, and zirconium [31]. In the experiments, RDX with paraffin was investigated as the reference material. The pressed mixtures (as strands) were burned in a window bomb under air atmosphere and under pure nitrogen at 0.3 MPa. The combustion was investigated using a high-speed color camera, equipped with a macro lens and fast scanning emission spectrometers operating in the range of 300 nm–14 μm . The data were collected and analyzed to characterize different reaction zones, to identify the intermediate metal oxides and final reaction products and combustion temperatures of condensed particles and gaseous species (like water, and di-at. fuel oxides) formed during the transient combustion process as function of time and position [31]. In the study, the different temperatures of reacting surfaces, particles and reaction gas(es) were considered as main parameters to characterize the reaction of fuel particles with RDX and additional air. The results have been discussed in comparison to qualitative reaction kinetic and to thermodynamic equilibrium calculations with EKVI and ICT-Thermodynamic Codes. The study showed a kind of ranking according to different applications and the effect of air. In some cases the additional air resulted in a temperature increase of several hundred kelvin. However, this effect is not only affected by the chemistry of the filler but also by other factors, like the particle size (those are also discussed in the paper) [31].

Sheridan et al. studied and patented a thermobaric munition including a composite explosive material, the composite

explosive material having a high explosive composition and a detonable energetic material dispersed within the high-explosive composition [55]. The detonable energetic materials investigated were in the form of a thin film, the thin film having at least one layer composed at least in part by a reducing metal and at least one layer composed at least in part by a metal oxide. The work included tailoring the blast characteristics of high explosive composition to match a predetermined time-pressure impulse.

Anderson et al. considered the detonation properties of combined-effects explosives [56]. In the development of new explosives, it is quite often necessary to balance a number of factors contributing to performance while certain formulation constraints exist. In that sense, statistical design of experiments (DOE) is a valuable tool for rapid formulation optimization and minimization of hazardous and costly testings. During the development of metal-loaded explosives, designed for the enhanced blast, it was discovered that upon proper formulation, aluminum additives gave full reaction accompanied by volume expansions, which resulted in extremely high Gurney energies equivalent to explosives LX-14 and PBXN-5 but with lower loading of nitramines. The early aluminum oxidation can be described by eigenvalue type detonations, where the fully reacted Hugoniot of the condensed phase aluminum oxide and explosive products lies below the unreacted aluminum Hugoniot. Such an analysis describes fully the agreement of aluminum consumption and volume expansions from 1-in. copper cylinder expansion tests and an analytic cylinder model, as well as detonation calorimetry with the early reaction of aluminum that also causes a shift in the gaseous reaction products to higher enthalpy species, such as CO and H₂, thus leading to further improvement in the direction of augmentation of blast. Hence, both the mechanical energy (for fragmentation or “metal-pushing”) and blast (for structural targets) are available in a single explosive fill. Note that this provides capability for combined metal-pushing and blast in a single explosive that was not previously possible [56].

Multi-walled active explosive charges (especially the hollow charges that contain hollow chambers within the explosives) contain metal carbonyls, either as pure substances or granules, that are mixed with the inorganic fuels and are integrated within the closed container of the explosive charge. Zimmermann patented some suitable metal carbonyls, which are considered as non-directional blast enhancers. They consist of Cr(CO)₆, W(CO)₆, Mo(CO)₆, Fe(CO)₅, Fe₂(CO)₉, and Fe₃(CO)₁₂ [34]. It was claimed that the charges having those carbonyls can be used for guided or unguided munitions or for gun ammunition.

It has to be mentioned that the search for novel and adaptive energetic materials requires innovative combinations between the particle technology and nanotechnology [57].

Nowadays nanomaterials are the focus of increased interest, since they possess some properties which highly differ from their macroscopic counterparts. Many applications recently take the advantage of possession of the new functionalities and manufactured nanoparticles [57]. In the recent years more attention has been paid not only to amelioration of the micro-structure of the energetic materials but also to the search of

possible modifications of materials that can be achieved by the application of proper coatings [58,59]. Parallel to these developments, the research on energetic nanomaterials is getting more and more attention. Beside the synthesis of energetic nanomaterials, another area of interest is the coating of energetic (nano)powders, in order to be able to modify their properties or to add new functionalities to these particles. Modified energetic materials find various applications in explosives, such as rocket and gun propellants, and pyrotechnic devices, etc. The modified energetic materials are expected to yield enhanced properties, e.g., enhanced blast, a lower vulnerability toward shock initiation, enhanced shelf-life and environmentally friendly replacements of the currently used materials. An experimental setup for coating of the existing powders was designed and constructed [57]. The experimental technique is based on a special plasma application which, contrary to more general plasmas, can be operated at relatively low temperatures and ambient pressure. This allows the handling of heat-sensitive materials, otherwise they would readily decompose or react at higher temperatures. The facility used for the coating of energetic powders in the lower micron range is based on a fluidized bed reactor in which the powder circulates. In this paper, an experimental technique was described in which CuO powders that were coated with a very thin, nanoscale deposit of a SiO-containing layer were tested first [57].

As mentioned above, this paper describes an experimental set-up in which a plasma reactor has been combined with a fluidized bed [57]. Although this combination is known in the literature, it uses relatively cold plasma which allows the processing of several tens up to one hundred grams of heat-sensitive materials, primarily energetic materials. The applications can obviously be extended to other heat-sensitive materials, like pharmaceuticals. The expected advantage of the plasma coating technique in combination with the fluidized bed is the formation of a thin and homogeneous coating layer around particles. It is expected that the coated materials will show different properties compared to conventional particles or physical mixtures of different particles. First trials with the coating of CuO particles with a polydimethyl siloxane containing layer indeed confirm a change from hydrophilic to hydrophobic properties of the powder as a result of the plasma treatment. Scanning He-ion microscopy (SHIM) and scanning electron microscopy (SEM) were applied to characterize the samples. Especially SHIM showed the presence of very small, droplet-like deposits on the CuO particles, with nanoscale dimensions (10–20 nm). The CuO samples treated during a longer time show indications of a thicker deposited layer. X-ray microanalysis has confirmed the presence of Si atoms on the surface of the treated CuO samples. As a next step, their intention was to further extend the work to include other materials, e.g. aluminum particles and energetic materials like explosives (RDX, HMX) or oxidizers (AP), metal/metal oxides combinations (thermites). The coated particles would be characterized regarding the coating efficiency, coating layer thickness, compatibility, reactivity, thermal properties, etc. The final goal would be to apply the coated materials in either explosive, propellant or pyrotechnic compositions in order to assess their

properties (performance, munition effects, enhanced blast, etc.) compared to conventional formulations.

The development of new energetic materials with enhanced-blast properties requires better understanding of the factors such as particle type, size and particle/matrix distribution. The article by Abadjieva et al. concentrates on coating of particles which opens new horizons and possibilities in energetic materials engineering [60]. Functionalities as ingredient compatibility, increased burning rates, and accelerated or delayed ignition become possible upon applying suitable coatings. The development and production of a new class of shock-insensitive, blast-enhanced explosives based on modified/functionalized (energetic) materials require new technologies. The authors described a research program briefly. The program included, e.g., the development of coated materials like aluminum powder. Using plasma-enhanced chemical vapor deposition (PECVD) technology, test powder was coated with SiO_x containing layers (with HMDSO as a precursor) and fluorinated layers (with C₂F₆ as a precursor). The results were presented and discussed in the article [60].

Lips et al. in their paper presented the development of an enhanced SIBEX (shock-insensitive blast-enhanced explosives) explosive formulation with optimized properties to suit a man-portable weapon system with anti-structure capability [61]. The development mentioned includes the down selection of four chemically and physically different SIBEX types. Also Lips et al. presented analysis assessment together with open-field testings.

Enhanced-blast charges gain more and more attention especially in connection with hard target defeat applications. The IHE needs both a good blast performance and also a veritable resistivity against high shocks during the perforation of a target. The new and appropriate acronym “SIBEX” (Shock-Insensitive Blast-Enhanced Explosive) has been created for these kinds of high explosives. In the course of a research program to design compositions with enhanced blast output, a variety of charges have been fired in a detonation chamber [32]. The quasi-static pressure build-up was measured as the only criterion for performance and the primary shock wave has been disregarded. All the charges were loaded with a high portion of micron-sized metal particles (usually aluminum and/or boron). The pressure did not always build up until it reached the equilibrium pressure, thus indicating that not all of the metal powder burned within the relevant time frame. By comparing simple composite charges (RDX/Metal/Binder) with shock-dispersed fuel (SDF) charges (comprising a center core made of a brisant explosive and a fuel-rich wrapping), it turned out that with SDF charges the pressure buildup was considerably faster. Some of the highly metalized charges reached a TNT equivalence lying between 1.5 and 1.7, on a performance scale relative to TNT and a quasi-static pressure developed far beyond that of the known explosives currently in service. In those tests, it could be shown that the supply of oxygen, i.e. the mixing of fuel with air, is the limiting factor in fast pressure build-up. For improvements of the performance further, the burning not only has to be enhanced particularly, but any means of accelerating the mixing are required as well.

The compositions of different energetic metallic particles and corresponding coatings are chosen in order to take advantage of the resulting exothermic reactions of alloying when the metals are combined or alloyed through heat activation. Bimetallic particles composed of a core/shell type structure of having different metals are to be properly chosen so that upon achieving the melting point (for at least one of the metals) a relatively great deal of exothermic heat of alloying is liberated. In a typical embodiment, the core metal is aluminum and the shell metal is nickel. Throughout the coating process the nickel may be deposited onto the outer surface of the aluminum particles by using an electrolysis process of a suitable metal salt solution with a reducing agent in an aqueous solution or a solvent media. The aluminum particles may be pretreated with zinc to remove any aluminum oxide present on the surface. The resulting bimetallic particles may be utilized as an enhanced blast additive by being dispersed within an explosive material [33]. The core metal can be one of aluminum, magnesium, boron, silicon, hafnium, or carbon. The outer shell metal is from nickel, zirconium, boron, titanium, sulfur, selenium, or vanadium. In the first stage of the procedure, 11 mL of zincate solution is mixed (a zinc gluconate solution having an approximately pH of 13) with 100 mL of deionized water. In the next step, the solution is stirred rapidly (with a magnetic PTFE stirbar) and the solution is brought to 65 °C. Then 0.25 g of aluminum powder composite is added (specifically, the grade H-60 aluminum powder). Then, the solution is stirred for 45 s, and vacuum filtered through a 1.2 µm PTFE membrane. Finally, the collected zinc coated aluminum particles are rinsed with deionized water. In the second stage, those pretreated aluminum particles are nickel plated. For this step, 30 mL of nickel sulfate is mixed with 90 mL of solution B (sodium hypophosphite), stirred with a PTFE coated stirbar and then heated to approximately 90–95 °C. Next, 0.29 g of the zinc treated aluminum powder is added and this temperature is maintained and the mixture is stirred until the appropriate amount of nickel is deposited. Then the solution is vacuum filtered through a 1.2 µm PTFE membrane. Finally, the collected aluminum core/nickel shell particles are rinsed with water, and then allowed to dry. The explosive material may be any type of explosive material that can mix with the bimetallic particles of the present invention as an enhanced-blast additive, e.g., octogen (HMX), hexahydrotrinitrotriazine (RDX), pentaerythritol tetranitrate (PETN), picrate salts and esters, dinitrobenzofuroxan and its salts, hexanitrohexaazaisowurtzitane (C-20), trinitrotoluene (TNT), glycidyl azide polymer (GAP), diazodinitrophenol (DDNP), lead azide and other azide salts, lead styphnate and other styphnate salts, triaminoguanidine nitrate, tetranitrodibenzole trazapentalente, diaminohexanitrophenyl, triaminotrinitrotoluene (TATB), or plastic bonded explosives (PBX) [33].

A processing technique was demonstrated by Vasylykiv et al., which was based on the synthesis of ceramic nanopowders and simultaneous impregnation with metallic nanoparticles by multiple “nano-blasts” of embedded cyclotrimethylene trinitramine (RDX) in preliminary engineered multi-component nano-reactors [62]. The “nano-blasts” of impregnated RDX

deagglomerate the nanopowder due to the high energetic impacts of the blast waves, while in the decomposition of compounds, their solid-solubility is enhanced by the extremely high local temperature generated during the nano-explosions. The investigators applied this technique to produce nanosized agglomerate-free 8 mol% yttria-doped cubic zirconia aggregates with an average size of 53 nm impregnated with 10 mass% of platinum particles of 2–14 nm.

The same authors also published a similar article to demonstrate a unique processing technique which was based on engineering of the multi-component ceramic nanopowders and composites with precise morphology by nano-explosive deagglomeration/calcinations [63]. As mentioned above, multiple nanoexplosions of impregnated cyclotrimethylene trinitramine (RDX) deagglomerate the nanopowder (due to the highly energetic impacts of the blast waves) while the solid-solubility of one component into the other is enhanced by the extremely high local temperature generated during the nano-explosions. They applied this technique to produce nanosize agglomerate-free ceriagadolonia solid solution powder with uniform morphology and an average aggregate size of 32 nm, and as mentioned before, 8 mol% yttria-doped zirconia aggregates with an average size of 53 nm impregnated with platinum (2–14 nm).

Lin et al. investigated the explosion characteristics of nano-aluminum powders with particle sizes of 35, 75, and 100 nm in a 20-liter spherical explosion chamber [64]. The results have indicated that the maximum explosion pressure and the maximum rate of pressure rise mainly depend on the dust concentration. For dust concentrations below 1000 g/m³, the maximum explosion pressure increases gradually to a maximum value with increasing the dust concentration, whereas after the dust concentration increases above 1250 g/m³, the maximum explosion pressure starts to decrease. The trends of the maximum rate of pressure rise follow the same pattern with increasing dust concentration. They found the lower explosion concentration limits of nano-aluminum powders with sizes of 35, 75, and 100 nm as to be 5, 10, and 10 g/m³, respectively, whereas the lower explosion concentration limit of ordinary aluminum powders is about 50 g/m³.

The investigation has revealed that:

- 1) For the nano-aluminum powders, the maximum explosion pressure was higher approximately by 0.2 MPa than that of ordinary aluminum powders at the same dust concentrations. Meanwhile, the maximum explosion rate of pressure rise for the nano-aluminum powders was found to be higher than that of ordinary aluminum powders by a factor of 2 to 6.5.
- 2) The lower explosion concentration limits of the nano-aluminum powders with particle sizes of 35, 75, and 100 nm were found to be 5, 10, and 10 g/m³, respectively. These values were far lower than those of the ordinary aluminum powders (50 g/m³).

The review article on cast aluminized explosives by Vadhe et al. considers the thermobaric PBX compositions [65]. Thermobaric (TB) compositions are most suitable to modern warfare threats. Indian researchers (the Naval Surface Warfare

Table 1
Explosive compositions considered.

Explosive	Composition	ρ /(g · cm ⁻³)
PBXIH-135	HMX/Al/HTPB	1.68
PBXIH-135EB	HMX/Al/PCP-TMETN	1.79
PBXIH-136	RDX/AP/Al/PCP-TMETN	2.03
PBXIH-18	HMX/Al/Hytemperature/DOA	1.92
PBXIH-18 mod. 1	HMX/Al/Hytemperature/DOA	1.77
PBXIH-18 mod. 2	HMX/Al/Hytemperature/DOA	1.84
HAS-4	HMX/Al/HTPB	1.65
HAS-4 EB	HMX/Al/PCP-TMETN	1.73
Talley Mix 5672	Al/Zr/IPN/Ethyl Cellulose (32/40/26.75/1.25)	2.21

Excerpted from Reference [65].

Center Indian Head Division (NSWC IHD) and the Talley Defense Systems (TDS)) developed some solid thermobaric compositions containing a moderate-to high aluminum content for lightweight shoulder-launched penetrating or anti-cave warhead for the M72 LAW system [66]. Various compositions which they developed with PBXIH-135 as the baseline composition are summarized below (Table 1). The composition, PBXIH-135 (HMX/Al/Poly urethane) present in Table 1, is one of the best examples categorized under thermobaric warhead systems. Thus, these insensitive munitions can be used effectively against bunkers, hard surfaces, tunnels and caves. It is worth mentioning that supersonic missiles and bombfill of the “General Purpose” category (500 and 2000 pound) demand insensitive munitions.

Hall and Knowlton [67] reported some thermobaric compositions based on wax, HTPB, or GAP as a binder. The challenge of their study was to determine comparative thermobaric characteristics for some chosen compositions in confined tests. They observed the highest impulse and average peak pressure for GAP based compositions. Ti/HTPB based compositions have been found to be superior to the corresponding aluminum-based compositions in terms of the average peak pressure and impulse. The abovementioned researchers also studied compositions containing GAP in combination with propriety energetic plasticizers and achieved the average impulse up to 975 kPa.msec. Hall and Knowlton [67] also reported gelled thermobaric compositions incorporating 60–70% Mg/Al/Ti/Zr as a fuel with 20–30% energetic liquid nitromethane (NM) and isopropyl nitrate (IPN). The NM-based compositions exhibited a higher impulse, as compared to IPN-based compositions. Also AN/AP/HMX composites were incorporated as oxidizer/energetic components. The researchers found some compatibility for all the combinations. The best results were obtained with the 30/30/40 NM/Al/HMX combination in terms of the average peak pressure (0.5 MPa) and average impulse (802 kPa.msec) [67].

The thermobaric weapons are employed to produce pressure and heat effects instead of armor penetrating or fragmentation damage effects [5]. These weapons as mentioned before are particularly effective in enclosed spaces such as tunnels, buildings, and field fortifications [1,68]. Their reactivity requires aluminum (or other reactive metals) to be employed in

explosive ordnance in the form of fine powder (added to explosives) to enhance their blast effect [65,69]. Generally, the main affection of the large aluminum mass fraction improves spatial mixing of components in explosives with oxidizing gases in the detonation products, thus resulting in the release of more efficient afterburning energy. However, the effect of aluminum in thermobaric explosives has been well identified; the high ignition temperature of aluminum is a key step in its application in TBXs. It is known that the reaction of aluminum and oxygen is affected by various factors such as the dispersion of aluminum particles, the scale of the aluminum particles or the coated/uncoated particles. Investigations have focused to improve the whole impact of TBXs. Hence, the search for additional materials which can release high enthalpy like aluminum [11] is a promising strategy to improve the energy of TBXs. Mechanistically, the reaction of a thermobaric explosive is divided into three stages and the parameter σ is introduced to explain the differences of the three stages. Because the combustion and detonation of TBXs do not only rely on chemistry, but also are affected by a lot of other parameters such as the charge mass, charge geometry, etc., there are various thermobaric models introduced into the literature to simulate the propagation of the detonation products with the surrounding environment. Xing et al. in their paper emphasize the basic theory of the reaction mechanism of TBXs. Concentrating on the relative details on the explosion of TBXs with aluminum, the parameter, σ , for TBXs was defined as [5]

$$\sigma = \Delta V / V - \beta \Delta H / C_p$$

where C_p is the heat capacity at constant pressure, ΔH is the heat changing term when the reaction proceeds, β is the thermal expansion coefficient and V is the volume of the system. According to the theory on flow in a reactive medium [70], parameter σ reflects the rate of transformation of chemical bond energy to molecular and bulk translation energy. Note that the parameter σ is introduced to estimate the detonation occurrence. By this method, the first stage is a detonation process in contrast to the last stage. This is in coincidence to the experimental phenomenon that the third stage of the process is afterburning. Actually, the mixture is heated up by the detonation process and the afterburning process becomes intense when the detonation processes finish. However, one should keep in mind that the confined environment is as important as the ignition temperature factor in the explosion of TBXs.

Some novel “high-blast”, or thermobaric, explosives were tested by Schaefer and Nicolich as potential replacements for the more conventional iso-propyl nitrate-magnesium mixtures [4]. However, high-blast explosives produce a moderate, long-lasting pressure wave that travels down corridors, around corners and through doorways. Hence, these explosives resemble fuel-air explosives more than the ideal high explosives. High-blast, or thermobaric, explosives initially disseminate the under-oxidized detonation products and the unreacted fuel into the ambient air. Then the mixture of fuel and ambient oxygen self-ignites to create an explosion with a long pressure wave. In the work of Schaefer and Nicolich, various formula-

tions were examined at several binder systems, with different high explosives, and metal-fuel types, in different sizes, and shapes, in which the reaction was kept slow enough to disperse the fuel but not so slow as to dissipate and extinguish itself [4]. The cast-cured explosives of high explosives and metal-fuels in a binder were capable of meeting the project goals. The cured binder system disperses well and creates desirable detonation products that easily undergo combustion. It has been found that the Mg-Al alloy represents a good low-temperature initiator and is necessary for a good performance. The intimate contact between these two metals in the alloy should be a likely reason that these formulations work better than those containing boron or titanium. It was observed that flake form of aluminum yields better outcome than spherical aluminum. The authors reported that in their work, metals like boron, titanium, and thermites did not help performance; similarly, neither CL-20 nor TNAZ worked as well as HMX or RDX [4].

8. Tests and methods

In the development and engineering of weapons and energetic materials various tests are to be performed. Su et al. provided a method for quantitative evaluation of energy release of thermobaric explosives based on implosion test [71]. The method determines the temperature and pressure to get the quality of explosives, the amount of oxygen needed for explosives to meet the requirements, the quasi-static pressure inside the tank to get quasi-static pressure peaks of thermobaric explosives, and finally to get the thermobaric explosive effect of temperature and pressure tests.

In their article, Li et al. have described a similar invention that is helpful in the field of explosives and provide a testing method again based on implosion tests for quantitative evaluation of thermobaric effect of thermobaric explosives [72]. Using pressure sensors, thermocouples and baseline TNT, the test method enables one to evaluate the temperature and pressure of explosion in the tank, the explosion overpressure curve, thermocouple temperature response curve, and quasi-static pressure curve (inside the tank). Then by the test data processing, the peak overpressure, response thermocouple temperature peak, impulse, quasi-static pressure peaks, calculated temperature, pressure characteristic parameters of TNT to explosives ratio, the temperature and pressure effects of temperature and pressure evaluation of explosives have been obtained. The described present invention uses an explosive canister as an evaluation test vehicle and TNT with the same quality as the base. Then, it evaluates quantitatively the thermobaric effect and provides technical basis for development of a thermobaric warhead and evaluating explosive power.

Zhong et al. described a multi-wavelength temperature-measuring system based on the atomic emission spectroscopy to measure the transient high temperature during the explosion process of thermobaric explosives [73]. The time resolution of the measurement system could be achieved in μs scale. In the experiments, by measuring the explosion temperature of thermobaric explosives, Zhong et al. managed to obtain the curves of temperature vs. time relation. There exist two temperature peaks corresponding to the oxygen-free reaction and

oxygen dependent reaction phases of the thermobaric explosive explosion process, respectively. The results showed that the relative error of the measured temperature is less than 2.6%, supporting a good repeatability. As compared with the double line of atomic emission spectroscopy, the multi-wavelength temperature-measuring system described in the study can minimize the errors resulting from the selection of spectral lines.

Through the years, aside from chemical weapons, warheads have also been designed to generate either fragments or blast shock waves as their primary damage mechanism. Thermobaric explosives (TBXs) have been predominantly used in a blast role (rather than for their fragmentation characteristics) due to their enhanced blast effect, which is a direct result of the secondary combustion of additives [74]. The shock wave generated by the detonation of TBXs is of a lower amplitude but has a longer period than that of conventional secondary explosives.

The work by Jaansalu and coworkers dwells on an investigation in which using a flash X-ray imaging technique, the ability of TBXs to shatter metal casings and to propel the resulting fragments have been reported [74]. During the investigation, three casing materials were used. Those were AISI 1026 steel, gray cast iron and ductile iron while two different TBX compositions were employed with C4 serving as a benchmark. The fracture behavior of the casings, as a function of explosive fill and material characteristics, was mostly as expected. They used C4 (RDX/plasticizer (91/9)), TBX-1 (monopropellant/magnesium) and TBX-3 (monopropellant/aluminum/RDX). One TBX formulation exhibited a run distance to detonation. The well known Gurney equation was employed to get a correlation and compare the final fragment velocities. It was found that in the case of two of these TBX compositions, as compared to similar amount of C4, a larger fraction of the available energy of explosive was converted to mechanical energy to propel the fragments. This fraction of energy was influenced by the confinement of the detonation products as well as the ignition delay of the metal powders. These two factors had a greater influence on the fragment velocities than did material characteristics. Jaansalu et al. also investigated and discussed the fragmentation characteristics, influence of explosive material, fragmentation velocity, influence of casing thickness, etc. [74].

Within the testing experiments, the X-ray images captured the fracture behavior of the casings as a function of fill and material characteristics. The casings fragmented as expected. The X-ray images also provided information on the run-up distance of the explosive fills used. The run distance for the TBX-3 formulation, containing liquid monopropellant, aluminum powder, and RDX, is about 20 mm. The run distance for the TBX-1 formulation (monopropellant/magnesium) is less than 20 mm, such that no indications of asymmetric expansion are observed. Note that the Gurney equation assumes that the fraction of energy propelling the fragments of any charge is roughly the same. The results obtained in this work have been found to be consistent with the conclusion that a larger fraction of energy is available in TBX (liquid propellant/metal) formulations. Furthermore, this fraction of energy is dependent upon the confinement of the detonation products as well as the igni-

tion delay of the metal powders used. It has been firmly concluded that those two factors have a substantial influence on the fragment velocities of the casing than do its material characteristics [74].

In the investigation by Fair, a technique called “Twin Screw Extruder” (TSE) was used [75]. The failures in manufacturing of advanced explosives containing large amounts of metal powders to improve performance, such as PAX-3, have proven how difficult the production stage is. According to the article, the old manufacturing processes had low yield which resulted in a high cost per unit and questionable product uniformity. A group of researchers (TSE team) who were investigating the use of a TSE machine to mix and extrude an aluminum base explosive (PAX-3) was mentioned. The TSE team had successfully demonstrated this concept on a new formulation (coded 02-02-06). This material had been processed using a smaller concentration of green solvents in comparison to the conventional batch processing and additionally, the product was more uniform. The TSE method mentioned above uses a base material consisting of coated HMX (PAX-2 or PAX-2A), made by conventional means, and reprocessing it into its aluminized corollary. The article claims that this manufacturing process is extremely flexible, allowing for the reformulation of a base material into a number of different explosives with designed and tailored characteristics. It was also claimed that this new technology cut the cost of manufacturing. The loss of organic solvents to the environment and waste treatment requirements would also be greatly reduced. It is anticipated that the concentration of the organic solvents to be employed will be reduced by as much as 50% as compared to traditional batch processes [75].

Hahma et al. tested certain thermobaric explosives and described their TNT-equivalents [76]. Thermobaric charges with four different liquid fuels and several powder fuels were prepared and fired and their TNT equivalences in the open field were determined. The test results have showed that the shock wave component of thermobaric explosion mostly originated from anaerobic processes. The fuel component was deemed critical for the generation of a thermobaric explosion. Throughout the tests, only IPN (iso-propyl nitrate) demonstrated some advantageous properties and a reliable ignition of the fuel and metal powder components in all proportions tested. IPN was also found to be the only fuel able to create effective, aerobic explosions even with excessive amounts of metal powder producing enormous overpressure pulses. The powder fuel seemed to be critical for the ignition delay in the aerobic stage. The activated aluminum showed the most promising properties followed by Elektron (92:7:1 Mg-Al-Zn alloy), phosphorus and boron. Note that metal combustion rate is a critical parameter in generating high pressure levels in the aerobic stage.

According to Pahl and Kaneshige the temperature of the particles in thermobaric explosives is a parameter of importance in determining when and to what extent aluminum particles participate in the expanding detonation products cloud [77]. In this paper, an experimental technique using 2-color pyrometry was used to measure the temperature and its spatial variation. The details of the diagnostic technique was presented

along with the light intensity and estimated temperature data obtained from tests of certain aluminized-explosives [77].

The article by Trzciński and Maiz reviews the available literature on thermobaric explosives and enhanced-blast explosives (high-destructive explosives) [8]. These types of explosives are defined, and their common features and differences are shown. The review discussed the data excerpted from the literature based on various tests (including small scale tests, larger scale tests, blast ability tests, underground tests, closed chamber tests, sensitivity tests, cylinder tests, particle size tests, etc.).

Klahn et al. investigated spectroscopically the afterburn reactions during explosions of enhanced blast explosives in a detonation chamber and in free field experiments [78]. Via concatenation of the spectra of three different spectrometers, a wide spectral range is accessible for investigation. Hence, it fits to the thermal continuum as well as to the water emission bands of the spectra to estimate the combustion temperature and water vapor content which could be improved. Then, different charges can be characterized by the obtained combustion temperature and the reaction course.

Years long experience has indicated that metal-based reactive composites have great potential as energetic materials due to their high energy densities and potential uses as enhanced-blast materials. However, these materials can be difficult to ignite with typical particle size ranges. Although mechanical activation of reactive powders increases their ignition sensitivity, it is not yet entirely understood how the role of refinement of microstructure due to the duration of mechanical activation influences the impact ignition and combustion behavior of these materials. Mason et al. studied impact ignition and combustion behavior of mechanically-compacted activated Ni/Al reactive powder in one of their work on microstructure refinement by using a modified assay shear impact experiment [79]. They obtained some properties such as the impact ignition threshold, combustion velocity and ignition delay time, as a function of milling period. It was found that the mechanical impact ignition threshold decreases from an impact energy of greater than 500 J to an impact energy of ca. 50 J as the dry milling time increases. It was observed that during the mechanical activation process the largest jump in the sensitivity was between the dry milling period of 25% of the critical reaction milling time (t_{cr}) (4.25 min) and 50% t_{cr} (8.5 min), corresponding to the time at which nanolaminate structures begin to form. The differential scanning calorimetry analysis have indicated that this jump in the sensitivity to thermal and mechanical impact was dictated by the formation of nanolaminate structures, which reduce the temperature needed to begin the dissolution of nickel into aluminum. It was shown that a milling time (of 50%–75% critical reaction milling time) may be near optimal when taking into account both the increased ignition sensitivity of mechanically-activated Ni/Al and potential loss in reaction energy for longer milling times applied. In the same range for all milling times considered which were less than the critical reaction milling time, some ignition delays were observed due to the formation of hotspots ranging from 1.2 to 6.5 ms. During the investigation the combustion velocities were found to be ranged from 20 to

23 cm/s for thermally-ignited samples and from 25 to 31 cm/s for impacted samples at an impact energy of 200–250 J [79].

The investigation of metal particles (nanometer sized) is important for various applications in blast enhanced explosives, particles in high performance ceramics and rocket propellants and pyrotechnics. Methods of thermal analysis are often applied to investigate the controlled compositions of metal particles also in various atmospheres. The results of various investigations based on methods of thermal analysis on the study reactions of Al and Ti particles in nitrogen as well as in carbon dioxide have been reported [80]. Aluminum reacts to form AlN in nitrogen and to Al_2O_3 in carbon dioxide; however it is delayed at higher temperature compared to a reaction in air. Ti also uses the residual oxygen in these atmospheres to form rutile structure in the case of nitrogen and it might in addition use carbon dioxide as an oxidizer. Both of them occur at higher temperatures compared to the compositions in air. The researchers attained some preliminary approaches to get some insights to mechanisms and kinetic parameters but these efforts do not currently give satisfying results; these efforts, however, might be successful in future work [80].

In 2006 the “afterburn effect” of SIBEX explosives (Shock Insensitive Blast enhanced Explosives) was simulated using the FEM code AUTODYN 6.1z. Unfortunately, the data library of AUTODYN 6.1z includes no material data and models of SIBEX. Evaluation of technical literature shows that up to a maximum of 15 ms after the detonation, the pressure behavior of SIBEX is similar to the behavior of conventional high explosives (example TNT). Shortly after the fumes, reactions seem to cause the appearance of the “afterburn effect”. Only TNT fumes were in the period of max. 15 ms after the detonation, and then these were simulated in different environments. TNT fumes simulations show that close to reflective surfaces of the room (walls, floor and/or ceiling) the fumes get a dynamic movement resulting to the pressure reflections (exchange/transfer of momentum) and the connected interexchange of impulse. Maximum 15 ms after the detonation, the fumes are located in the middle of the room, independent of the place of detonation in the room (with or without windows/doors). The dynamics of fumes in open air and inside of rooms are not the same. To validate the fumes dynamics, a test room was equipped with different measuring sensors. In collaboration with the German-French Research Institute Saint-Louis (ISL), the test room has been equipped not only with numerous pressure and temperature sensors, but also with high speed heat flux sensors for the first time. The parallel installation of the measuring sensors led researchers to determine exactly the hot fumes cloud. Meantime, optical validation tests were conducted at the Fraunhofer Ernst-Mach-Institute (EMI) using a laboratory scale (1:10) setup. The measurements and video recordings confirm, in principle, the existence of the fumes dynamics of TNT in the rooms and thus validate the simulation results of AUTODYN 6.1z. [81].

Generally the incorporation of solid fuel particles to explosive formulations reduces the detonation velocity but can enhance the blast performance. That is the case when prompt combustion of the particles occurs in the detonation products and the surrounding air is early enough to support the shock

[82]. The degree to which fuel particles burns effectively highly depends on their dispersal throughout the explosion field and on their access to oxidizers. To distinguish the factors affecting the dispersal of fuel particles from those controlling their combustion, the investigators began by analyzing the dispersal of equivalent mock inert particles [82]. For that purpose solid glass spheres embedded in detonating small explosive charges were monitored by using high-speed digital shadowgraphy. Two different sets of particle sizes, 3 and 30 μm , and different mass fractions in the explosive compositions were considered for testing. The shadowgraphs and pressure measurements obtained were compared to the predictions of a newly developed multiphase numerical model. Reactive aluminum particles in the range of 1–120 μm in diameter were also analyzed. It was observed that during the first 50 μs of the expansion, the general trend for both the reactive and inert particles is such that the smaller particles expand near or beyond the leading shock wave to a greater extent than the larger particles. Expansion beyond the initial shock from the detonation is presumed to occur when particles agglomerate. The results have been found to be consistent with the predictions of the numerical models, highlighting the contributions of simple factors such as particle size and density in the early time expansion and mixing of fuels for enhanced-blast applications [82].

The fireball characteristic parameters of the thermal-baric explosive (TBX) and conventional explosives were measured by the method of IR imaging technique by Kan et al. [83]. The data obtained indicate that the temperature and pressure of TBX explosives are much larger than conventional explosives. The occurrence of the secondary explosion of TBX was recorded by high speed camera. When the blast processes of TBX and Composition-B were compared, it was found that the secondary explosion has certain enhancement function on TBX blast fire-ball [83].

Note that the explosive compositions include separate acceptor and explosive phases. The acceptor phase contains a halogenated polymer and a reactive metal which are capable of reacting at high temperatures and pressures whereas the explosive phase includes a non-metalized explosive. A portion of the explosive phase surrounds the acceptor phase, and detonation of the explosive phase exposes the acceptor phase to high temperatures and pressures which permit the metal and halogenated polymer to react efficiently and produce much greater temperatures and pressures. The explosives produce a detonation pressure range greater than 200 kilobars at the Chapman–Jouget (C–J) condition [84]. Lund and Braithwaite consider explosives having enhanced air blast and some tests on them [84].

Baker et al. have described a methodology and an apparatus for the study of both detonation and deflagration characteristics of complex compositions, especially pyrotechnics. Those generally provide nonideal detonation, high-velocity deflagration, and various phenomena such as transitions from one to the other, as well as the effects of intrinsic factors such as particle size, stoichiometry, and sensitizer and inert additives and extrinsic factors such as initiation type and energy, size, and confinement [85]. The described apparatus was used to assess

compositions for blast-enhanced explosives as well as for insensitive-explosives.

The increased interest in thermobaric weapons has driven a need to develop and evaluate brand new thermobaric explosives (TBXs) more efficiently. For that purpose Nammo Talley company traditionally developed and evaluated TBXs using theoretical thermochemical codes on new compositions which was followed by a down-selection of potential candidates based on the results. In the experiments, one to two pounds of charges of the candidates were tested in an instrumented and reinforced-concrete enclosure to characterize thermobaric performance in the real-world. The researches claim that this approach has worked well when there was a series of several formulations to test. However, enclosure testing is costly when performing single evaluations due to the personnel required for setup, testing, and teardown. Furthermore, the thermochemical codes cannot always predict real-world TBX effects, which occasionally yields unexpected enclosure test results. Therefore, an opportunity was realized to develop a new method which was capable of characterizing thermobaric compositions better, before they were tested in the enclosure. For this aim, in 2005, Nammo Talley collaborated with Parr Instruments to design and fabricate a detonation calorimeter to aid in the development and evaluation of TBX. The detonation calorimeter can quickly and economically characterize gram-size TBX samples prior to testing in the enclosure. The detonation calorimeter, due to the adiabatic environment it provides, gives a more precise total energy output value than the enclosure. The energy released from a TBX detonation in the calorimeter under various atmosphere conditions can be readily quantified. The energetic contributions of both the detonation itself and subsequent combustion of the fuel rich detonation products and thermobaric fuels can be differentiated. This is useful in determining the effects of additional enhanced fuels to TBX compositions. To optimize the thermobaric performance, the company has tested a series of conventional explosives, enhanced blast compositions and some experimental thermobaric compositions. In this paper, Hall et al. discusses the development and operation of the detonation calorimeter and provides a summary of the test results for energetic compositions evaluated [86].

In the work of Li and Hui, the IR thermography method was used to investigate the detonation temperature of certain thermobaric explosives (TBE) [87]. The experimental results have showed that the temperature of TBE's detonation was higher than that of TNT with the same weight. The duration of high temperature and the volume (the high temperature) were 2–5 and 2–10 times as much as those of TNT, respectively. This implies that TBE is superior to the traditional high explosive on the temperature field. The high-temperature environment formed by the explosion is sufficient to maintain the afterburning of the aluminum powder, which can provide further assistance to boost up the blast wave.

Collet et al. have developed a specific model which is able to reproduce the experimental blast effects [54]. This model is claimed to reproduce the expansion of the detonation products in a room, as well as the shock wave reflections and the

interaction between detonation products and air leading to the formation of afterburning products. This model was called DECO (detonation combustion). In order to be able to simulate large scale trials, in the study, the DECO was associated with an adaptive mesh refinement (AMR) technique. This coupling enables one to simulate the behavior of detonation products generated by 1 kg of explosive in $8 \times 8 \times 8 \text{ m}^3$ room with a reasonable number of nodes.

Lips et al. in their study investigated the development of an enhanced SIBEX (shock-insensitive blast-enhanced explosives) explosive formulation with optimized properties to suit a man-portable weapon system with anti-structure capability [61]. The development includes the downselection of four chemically and physically different SIBEX types having analysis assessment together with open-field testing.

In the work of Triciński et al., the confined explosion of an annular layered charge composed of a phlegmatized RDX (RDXph) core and an external layer consisting of aluminum powder or a mixture of ammonium perchlorate (AP) and aluminum was studied [9]. Experiments were carried out in entirely and partially closed structures, i.e., in the explosion chamber of 150 dm^3 in volume and in the 40 m^3 volume bunker with four small holes and a doorway. In the mixtures, two types of aluminum powder were used. The overpressure signals from two piezoelectric gauges located at the chamber wall were recorded and the influence of aluminum contents and particle size effect on a quasi-static pressure (QSP) were studied. Moreover, the solid residues from the chamber were analyzed by using SEM, TG/DTA and XRD techniques to determine their composition and structure. The pressure and light histories of the samples recorded in the bunker enable the researchers to determine the blast wave characteristics and time-duration of light output. The effect of the charge mass and aluminum particle size on blast wave parameters were investigated. For comparison, tests for phlegmatized RDX (RDXph) and TNT charges were also carried out.

The so called “layered-charges” consist of cylindrically loaded layers of energetic materials. Usually a core charge is a classic high explosive and outer layers consist of a mixture of fuel and oxidizer or the fuel itself [11,88,89]. Such materials are classified as enhanced-blast explosives (EBX) or thermobaric explosives (TBX). The fuel burning in the products of detonation or oxygen from the air raises the temperature of the cloud of gaseous products and strengthens the blast wave. Differences between the effects of the explosion of TBX and EBX are usually small and therefore these terms are often used interchangeably. However, since EBX is primarily for strengthening blast wave, while TBX is for providing an increase in temperature and pressure of the explosion, the classification of charges to a specific type depends on how the fuel is burned after the ending of the detonation. In materials like EBX, anaerobic combustion reactions, (or combustion without oxygen from the air) occurs. This means that after passing of the detonation wave, most of the fuel burns in atmosphere of the products of detonation. In materials like TBX, reactions of the fuel and oxygen from the air dominate. This process is described as aerobic burning [52,75].

Analysis of the results obtained in the work involving layered-charges leads to the following conclusions:

- 1) The parameters of the incident blast wave increased by only 25–30% after the explosion of larger layered-charges inside the bunker despite the fact that the charge weight increased twice.
- 2) The blast wave parameters increase with the increase of aluminum contents, particularly in the case of charges with larger diameter core. This means that burning of aluminum and additional heat strengthen the blast wave already during the detonation products’ expansion.
- 3) Due to the dynamic changes in overpressure the question as to how the particle size of aluminum affected the blast wave parameters of the tested charges was not answered.
- 4) The increase in the total pressure impulse in the bunker (determined for the time of about 40 ms) for almost all large charges was about 80–100% in relation to small charges weighing two times less. The highest impulses were obtained for charges with the outer layer of pure-aluminum powder.
- 5) Light output time of explosion of the layered-charges was 3–4 times longer than the RDXph core.
- 6) As compared to the core, the application of the outer layer in the charges caused twofold increase in quasi-static pressure inside the chamber filled with air.
- 7) The values of a ratio of the quasi-static pressure to the average pressure obtained from thermochemical calculation showed that only part of the aluminum burned up during the measurement time of overpressure in the chamber (40 ms).
- 8) Lack of oxygen from air caused the quasi-static pressure (QSP) in the chamber filled with argon to decrease with increasing aluminum contents in mixtures with AP.
- 9) From the TG/DTA and XRD analysis of the chamber residue it follows that the aluminum powder is almost completely burned after the explosion of the layered-charges in air.

The characterization of the properties of blast enhanced explosives, and in particular the mechanisms involved in the secondary reaction phase, requires the application of specially adjusted measurement techniques. Besides the standard pressure and blast measurement techniques, the Fraunhofer Institute for Chemical Technology (ICT) applies a variety of optical and spectroscopic methods like emission spectroscopy and Background Oriented Schlieren (BOS) methods. In addition, thermodynamic calculations are used to select powerful enhanced-blast explosive formulations. Several characterization methods and techniques have been presented by Kessler et al. [90].

In order to improve understanding of how aluminum contributes in non-ideal explosive mixtures, cast-cured formulations have been analyzed in a series of cylinder tests and plate-pushing experiments [7]. This study of Manner et al. describes the contribution of 15% aluminum (median size of 3.2 mm) vs. lithium fluoride (an inert substitute for aluminum; <5 mm) in cast-cured HMX formulations in different temperature regimes. Experimentally, small cylinder tests were performed to analyze

the detonation and wall velocities (1–20 ms) for these formulations. Near-field blast effects of 58 mm diameter spherical charges were measured at 152 mm and 254 mm using steel plate acceleration. Pressure measurements at 1.52 m gave information about free-field pressure at several milliseconds. While the observed detonation velocities for all formulations were within uncertainty, significantly higher cylinder wall velocities, plate velocities, and pressures were observed for the aluminum formulations at or greater than 2 ms.

Actually, in the work, they have studied the detonation and post-detonation environment for a series of cast-cured formulations using HMX and aluminum or LiF as an inert substitute. Using cylinder tests and plate-pushing experiments, they have been able to map out the effects of aluminum reactions in three different temperature and experimental regimes, from 1 ms to 1.8 ms. In the cylinder tests, no significant difference was observed in detonation velocities between the aluminum and LiF-containing formulations, and the measured cylinder wall velocities for HMX-Al and HMX-LiF were identical at 1 ms. However, at 2 ms, wall velocity was 13% higher for HMX-Al than for HMX-LiF, and increased to 20% at 20 ms. The plate tests were performed to observe blast effects and aluminum reactions at longer timescales (100–200 ms), and the measured plate velocities were up to 31% higher for HMX-Al than for HMX-LiF. The free field pressure measurements showed 38% higher pressures for HMX-Al than for HMX-LiF at 1.52 m (1.5 and 1.8 ms). Overall, this work shows that aluminum reactions in HMX explosives can occur as early as 2 ms and may continue to increase expansion as late as several milliseconds [7]. Collectively, this work gives a clearer picture of how aluminum contributes to detonation on timescales from 1 ms to about 2 ms, and how the post-detonation energy release contributes to wall velocities and blast effects. The experiments have indicated that significant aluminum reactions occur after the CJ plane and continue to contribute to expansion at late times [7].

9. Calculations and modeling

Mohamed et al. have reported a novel approach for the chemical composition optimization using thermochemical calculations in order to achieve the highest explosion power [91]. Shock wave that resulted from thermobaric explosives (TBX) was simulated using ANSYS AUTODYN 2D hydrocode. Nanoscopic fuel-rich thermobaric charges were prepared by the pressing technique and static field tests were conducted. Comparative studies of modeled pressure-time histories to practical measurements were carried out. A good agreement between the numerical modeling and experimental measurements was observed, particularly in terms of the prediction of wider overpressure profile which is the main characteristics of TBX. The wider overpressure profile of TBX was ascribed to the secondary shock wave that resulted from fuel combustion. The shock wave duration time and its decay pattern were acceptably predicted by means of the calculations. Effective lethal fire-ball duration of 50 ms was achieved and evaluated using an image analysis technique. The extended fire-ball duration was correlated to the additional thermal loading due to active metal fuel combustion. The tailored thermobaric charge exhibited an

increase in the total impulse by 40–45% compared with reference charge [91].

Mohamed et al. also used Explo5 steady-state equilibrium program to calculate the explosive characteristics and performance parameters for a number of thermobaric explosive formulations based on mono propellant or nitromethane as an explosive filler and aluminum powder as a fuel metal. Based on the results of Explo5 program, three thermobaric compounds were selected and prepared in test cartridges of 5 kg for each. Blasting field area was designed to test three prepared thermobaric charges and a reference charge of the same weight. The pressure-time history, using 12 pressure transducers located at different distances from the explosion center was measured. The explosion events were monitored by a high speed camera while the pressure-time history was registered by data acquisition measuring system. Test results demonstrated that the positive phase impulse of the tested thermobaric explosive charges increased by 40–45% and 30–33% for formulation based on monopropellant and nitromethane, respectively, as compared with reference charge [92].

In the work of Zhong et al. the descriptive parameters of explosion fireball of a thermobaric explosive and TNT were measured by an IR imager. According to the experimental data, a dynamic model of fireball thermal radiation was studied, and the change of the size of fireball and its position were quantitatively described. Based on the dynamic model used, the thermal damages by the thermobaric explosive and TNT fireballs were analyzed. The results showed that the thermal dose of the thermobaric explosive was 3.6–4.8 times as much as that of TNT, which indicated that the thermobaric explosive had advantages in the thermal damage effect. Compared with a static model, the dynamic model was found to be more reasonable to estimate the thermal effect of explosive fireball since it could describe the movement of fireball [93].

Kim and Su reported a significant progress of the modeling and simulation for the secondary combustion of the thermobaric explosives (TBX) [94]. They developed some Eulerian–Lagrangian models for the detonating blast propagation as well as for the combustion of aluminum metal particles. Some experiments in a confined chamber and open field were carried out for the model validation and for the understanding of the important physics associated in TBX flow. The results showed that in the confined chamber, an excellent agreement of the pressure history was precisely validated and the secondary combustions by aluminum vapor were mostly contributed by the anaerobic reaction mechanism. By applying to open field application, they demonstrated that their developed modeling and simulation calculations were also capable of resolving the detailed blast propagation mechanisms and emphasizing that the aluminum burning law was the most important parameter for TBX performance [94].

The afterburning from explosion of a TNT charge containing aluminum particles (TNT/Al) at three “Heights of Blast” (HoB) was investigated in order to demonstrate that numerical simulations could facilitate evaluation of the performance of enhanced-blast explosives (EBX). The simulations were conducted by using a two-phase Large Eddy Simulation model in

Euler–Lagrange form, incorporating the interaction between phases by means of a two-way coupling. The “finite rate Arrhenius chemistry” is used for the purpose of simulating afterburning, hence enabling the examination of contributions of heat release from carbon and aluminum afterburning reactions. The simulation results have indicated that aluminum afterburning in EBX charges was dependent on the mixing intensity, which was established by instabilities through shock-mixing layer interaction. As the shock propagation pattern is different for all Heights of Blast, the mixing intensity in its turn varies with “Heights of Blast” [95].

Grys and Trzciński used the thermodynamic code (ZMWNI) for the determination of the chemical equilibrium composition of a non-ideal heterogeneous system [96]. Computations of combustion, detonation and explosion parameters for some explosives were performed and isentropes expansion of products and detonation energy were estimated. Moreover, the non-equilibrium calculations were carried out, in which various assumptions were done such as the chemical inertness of one from the components of explosive composition as well as no heat exchange between the components and the detonation products. At the end, some calculated detonation characteristics were compared with the experimental ones [96].

Grys and Trzciński also described in detail the thermochemical program ZMWNI that they used for the calculations. The results of exemplary calculations were presented to verify the ZMWNI program. The code can calculate the parameters of combustion, explosion and detonation of condensed energetic materials as well as determine the curve of expansion of detonation products in the form of JWL isentrope [97] and the energy of detonation [98]. Moreover, the ZMWNI code is presented as capable of determining the non-equilibrium states for frozen composition or for different temperature of components.

The results were compared with those obtained from the CHEETAH code. In particular, the calculated adiabatic combustion temperature, JWL isentrope and detonation energy were shown. Moreover, new possibilities of the program, i.e., the non-equilibrium calculations, are demonstrated. Finally, some experimental data are confronted with the results obtained from the ZMWNI calculations. In the last years some European standards have been implemented in Poland and they are recommended for determination of explosion and combustion parameters. The presented program enables one to calculate combustion, explosion and detonation characteristics, and it can be modified according to the procedures described in the standards.

In their work, Moxnes et al. first theoretically studied the different energetic measures of aluminized explosives by applying the rules of thermodynamics [35]. Thereafter, they applied a well-known thermodynamic computer code to calculate various energetic quantities at different aluminum contents and freezing temperature. Energy concepts for aluminized explosives such as the calorimetric energy of explosion, enthalpy of explosion, work of explosion and Gibbs free energy of explosion were analyzed and compared to experimental values. They also studied the work of Carnot which is relevant for thermobaric effects. It was found that for highly aluminized

explosives (e.g. 50% Al), the work of Carnot was of the same size as the work of explosion. They could conclude that neither of the quantities, such as change in free energy, enthalpy nor internal energy of explosion should be considered as good measures of effectiveness of aluminized explosives [35].

A great deal of effort has been made in parallel to numerical simulations. French researchers have developed a specific model which is able to reproduce the experimental blast effects [54]. This model can reproduce the expansion of the detonation products in a room, the shock wave reflections and the interaction between detonation products and air leading to the formation of afterburning products. This model was called DECO (detonation combustion). In order to be able to simulate large scale trials, the DECO was associated with an adaptive mesh refinement (AMR) technique. Thus, this coupling enabled Collet et al. to simulate the behavior of detonation products generated by 1 kg of explosive in $8 \times 8 \times 8 \text{ m}^3$ room with a reasonable number of nodes (4.106) [54].

On the other hand, while experimenting with SIBEX explosive, Lips et al. also numerically modeled and made some tests with it within a multi room bunker complex [61]. The results were analyzed and screened to an optimized SIBEX composition for application in a shoulder launched weapon (SLW) system.

Arnold and Rottenkolber, while studying combustion of boron-loaded explosives, applied a single phase hydrocode model with idealized kinetics (which had been previously developed) in order to model some of the detonation chamber trials [32]. Though the model is strictly applicable only to charges with fast-burning fuels, it was also applied to a charge with high boron content.

Manner et al. performed plate tests (as mentioned above) to observe blast effects and aluminum reactions at longer timescales (100–200 ms), and measured plate velocities up to 31% higher for HMX-Al than for HMX-LiF. The free field pressure measurements showed 38% higher pressures for HMX-Al than for HMX-LiF at 1.52 m (1.5 and 1.8 ms). They made CTH calculations for the plate velocities. The hydrocode calculations were performed to determine how non-ideal behavior affected the plate test results while trying to find out the role of aluminum in the detonation and post-detonation expansion of selected cast HMX-based explosives [7].

10. Epilogue

The present short review article considers thermobaric explosives (TBX) and enhanced blast explosives (EBX) and outlines various studies including their compositions, properties, and reactive metal components involved as well as studies on their modeling and computations, etc. These explosives of mentioned type constitute a sub-family of volumetric weapons. Differences between TBX and EBX are usually small and therefore often these two terms are used interchangeably. They are fuel-enriched heterogeneous explosives. Unlike ideal high explosives, they are designed to produce long-lasting pressure waves which are able to travel through corridors, propagate around corners and through obstacles. They are extremely effective and destructive in enclosed spaces due to their ability

to produce a high level of quasi-static pressure (QSP). A much higher total energy output is provided by TBX and EBX explosions compared to conventional explosives.

The explosion process of those types of explosives consists of three stages: initial stage, anaerobic stage, and aerobic stage. Both the kind and amount of the metals added to TBXs and EBXs are essential. Metal additives are influencing on the ignition temperatures of TBX and EBX type explosives. Aluminum has been used for this purpose for a long time. Although the precise reaction of aluminum with detonation products is not understood completely to this day, it is widely accepted that the consumption of aluminum takes place over a longer time scale, as compared to TNT, RDX, or HMX. The aluminum consumed on the sonic (Chapman–Jouguet) surface can support the detonation front. The positive effect is observed for high explosives both with positive or negative oxygen balance, provided that there is a higher content of hydrogen and a lower content of carbon in a molecule. Recently some other reactive metals alone or together with aluminum were employed in these explosives.

If the fundamental physical and chemical phenomena of TBX and EBX could be understood well and controlled effectively, various new weapon systems of significant efficiency may emerge and be available to the war-fighter in the future.

Abbreviations

AMR	adaptive mesh refinement
B/HMX	HMX-based explosive compositions
Δp	overpressure
DDNP	diazodinitrophenol
DECO	detonation combustion
DOE	design of explosives
EBX	enhanced blast explosive
ESD	electrostatic discharge
FAE	fuel-air explosives
GAP	glycidyl azide polymer
HE	high explosives
HoB	heights of blast
HTPB	hydroxy-terminated polybutadiene binder
IHE	insensitive high explosive
IM	insensitive munition
IM	insensitive munition
IPN	isopropyl nitrate
MA	mechanical activation/mechanically activated
MIC	thermites/intermolecular composites
PTFE	polytetrafluoroethylene
QSP	quasi-static pressure
RDXph	phlegmatized RDX
R-T	Rayleigh–Taylor
SDF	shock dispersed fuel
SFAE	solid fuel-air-explosive
SIBEX	shock insensitive blast enhanced explosives
TBX	thermobaric explosive
TMD	theoretical maximum density
TSE	twin screw extruder
TBE	thermobaric explosive

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